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STANDARDS DEVELOPMENT BRANCH (MDE)



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# ACIDIC PRECIPITATION IN ONTARIO STUDY

AN ASSESSMENT OF THE  
PERFORMANCE OF THE  
DAILY PRECIPITATION AND  
AIR SAMPLING MONITORING  
NETWORKS  
JULY, 1980 - DECEMBER, 1981

April 1985

ARB-100-85-AQM

API-20/85

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Ministry  
of the  
Environment

The Honourable  
Jim Bradley  
Minister

Rod McLeod, Q.C.  
Deputy Minister

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## **ACIDIC PRECIPITATION IN ONTARIO STUDY**

### **AN ASSESSMENT OF THE PERFORMANCE OF THE DAILY PRECIPITATION AND AIR SAMPLING MONITORING NETWORKS JULY, 1980 - DECEMBER, 1981**

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## 1.0 INTRODUCTION

This report assesses the performance of the daily precipitation and air sampling networks from July 1980 to December 1981. Details of the sampling equipment and protocols used in these networks are described in a separate report (1). Data reports for these periods have previously been published for both the daily precipitation network (2) and the daily air sampling network (3).

The daily precipitation network began partially operating during July 1980. The majority of sites were operational by December 1980 except for the Northwestern Region sites which started operating during the fall of 1981. Fully operational, 16 sites utilized Aerochem Metrics and SES (Sudbury Environmental Study) sampler types. The Aerochem Metrics (wet-only sampler) was the primary collector used for sampling in May to October (hereafter referred to as "summer" period) when precipitation was mainly in the form of rain; while the SES collector (bulk sampler) was used exclusively in November to April (hereafter referred to as "winter" period) for snow and rain collection. Precipitation depth measurements were taken at each site using an AES (Atmospheric Environment Service) standard rain gauge during the summer sampling periods and a Nipher-shielded snow gauge during the winter sampling periods. A site map is provided in figure 1.

Metrex sequential air samplers (Type SAS 8-25) are utilized in the daily air sampling network. This network consists of 4 sites. Collection of daily ambient air samples began in the Southwestern Region (Longwoods) on March 3, 1981, in the Central Region (Dorset) on July 25, 1980, in the Southeastern Region (Charleston Lake) on March 23, 1981, and in the Northwestern Region (Fernberg) on October 2, 1981. All samplers are loaded weekly with 7 active filter packs and 1 passive filter pack. Each active pack is exposed for 24 hours and the passive pack is used for passive loading corrections. A site map is provided in figure 2.

The performance assessments of both networks are based on field observations, data validation observations, site comparisons, and laboratory quality control (QC) data. The site numbers used in all figures and tables correspond to the site numbering found in the site maps (figures 1 and 2). Assessment summaries and recommendations for each network are provided at the end of the report.

## 2.0 PRECIPITATION NETWORK

The following sections assess the performance of the event precipitation monitoring network during 1980-81.

### 2.1 Field Observations

Field observations are appended to the sample records in the published data listings report (2) which reflect the conditions of the collected samples and any sampling problems which occurred during the collection period.

#### 2.1.1 Sampler Malfunctions

Evaluations in this section refer only to the Aerochem Metrics sampler. Since the SES sampler is a bulk sampler, it does not suffer from mechanical and electrical sampler malfunctions. Any sample coded in the data listings report (1) with an "F" (sampler malfunctioned), "I" (event missed), "J" (wet-side open when not precipitating) or "L" (part of event missed) is considered a malfunction in this evaluation.

Overall, sampler malfunctions averaged 5.7% (65 out of 1,138 samples) during 1980-81. Figure 3 shows the percentage of sampler malfunctions for every monitoring site (except for N.W. Region due to an insufficient sample size). The following sites had higher percentages of malfunctions compared to the rest of the network: Nithgrove (19.6%), Whitman Creek, (12.3%) and Charleston Lake (15.9%). Whitman Creek was operated by a battery power supply and experienced many problems during the winter period. There are no explanations for the higher percentage of sampler malfunctions at Nithgrove and Charleston Lake during the 1980-81 sampling period.

Figure 4 shows the percentage of sampler malfunctions on a monthly basis during 1981. The months of August and September accounted for over 61% of all sampler malfunctions.

### 2.1.2 Sample Leaks or Spills

Samples that leak or spill are coded "G". During 1980-81, 3.7% of all samples leaked or spilled. Figure 5 shows the percentage of leaks or spills for every monitoring site. Leaks are not expected to occur as frequently in the daily network as in the cumulative precipitation network (cumulative leak or spill site average  $\approx$  19%) since samples are collected on a daily basis and are not exposed to the freezing and thawing cycles over a monthly period (4).

Figure 6 shows the comparison of the percentage of leaks or spills on a monthly basis for the two monitoring networks (daily and monthly) during 1981. Over 64% of all leaks or spills in the daily network occurred during the months from November to April. Over 61% of all leaks or spills occurred during November to April in the cumulative precipitation network. Generally, in both networks the same pattern emerges with the most frequent occurrence of leaks or spills during the months of November, December and February. It is speculated that during January fewer freezing and thawing cycles occur thereby reducing the frequency of leaks in the sample bags.

### 2.1.3 Samples Lost or Not Submitted

Samples may not be submitted (coded E) to the laboratory for chemical analyses because of an insufficient volume (<10 mls) collected in the sampler. Similarly, a sampler malfunction may result in little or no sample collected. Overall, 5.4% of all collected samples (109 out of 2,034 samples) were not submitted for analyses. Figure 7 shows the percentage of samples not submitted for every monitoring site. All sites but Charleston Lake (12.5%) had fewer than 10% of collected samples not submitted. Collected samples from Charleston Lake were not submitted on 21 occasions out of 168 samples. Of these 21 samples, 17 were not submitted because of insufficient volume for analyses.

It should be noted that every site operator is expected to submit sample field sheets to indicate samples which are collected with



insufficient volume for analysis. These small precipitation events can only be known to have occurred if a field submission sheet is coded with the "insufficient volume" ( < 10 mls) and "not submitted" codes. If an operator does not submit field sheets with these codings, there will be no record in the database of these events.

Lost or misplaced samples are coded an "X" under office comments in the data listings report. Overall, less than 1% (13 out of 2,034) of all collected samples were lost during 1980-81. Of the 13 samples lost, 6 were lost during February 1981.

#### 2.1.4 Data Recovery

Data recovery is discussed within this section by using two approaches. The first method simply calculates the percentage of missing data. The majority of missing data usually results from the collection of small volume samples. Even though samples have been collected without any problems (ie. no sampler malfunctions, leaks, spills etc.) data are still missing for some particular events because of the lack of sufficient sample volume for a complete laboratory analysis. This is not a reflection of the network performance.

The second approach is to determine the number of sample collection "inconsistencies" between nearby monitoring sites. It is recognized that the spatial variability of precipitation will account for many of these inconsistencies since in most cases the distance between compared sites can be up to 10 kilometers or less. An inconsistency, in this context, is defined as a day in which only one of the two nearby sites collected a sample. This approach is used only to provide some means of comparison between sites and it could possibly shed some light on potential operating problems. These operating problems could be instrument sensitivity problems or operator problems such as failing to submit field sheets for trace precipitation amounts.

Figures 8 and 9 show the percentage of data recovered (100% - % missing data) during 1980-81 for every site. Using the Aerochem Metrics sampler, the percentage of data recovered from every site varied from 55.5% (North Easthope) to 87.8% (Dorset). Using the SES sampler, data recovery averages ranged from 58.4% (North Easthope) to 96.3%

(Wellesely). Using the Aerochem Metrics sampler, the average percentage of data recovered for all sites was 70.2% compared to 76.0% for the SES type sampler (combined sampler average is 72.7%). It should be noted that the SES collector was discontinued and replaced by the Aerochem Metrics collector for winter time sampling in the fall of 1982. The rationale for this change is discussed in section 2.2.1. It is expected that the percentage of data recovered will decrease during the winter sampling months using the Aerochem Metrics sampler. Since the SES sampler's opening is larger than the Aerochem Metrics, larger sample volumes are collected in the SES type hence minimizing the chance of not having adequate sample volumes for chemical analyses. The impact this change has on data recovery can only be evaluated by calculating the percentage of missing data during the winter sampling period of 1982.

Data recovery is calculated by parameter type for all stations combined in Table 1. In this table, data results coded as unreliable (section 2.2.4) have been excluded from the recovery calculations. Using the Aerochem Metrics sampler, better recovery percentages occurred for lab pH, sulphate, and nitrate parameters. This is expected since parameters are analysed on a priority basis if insufficient volume is available for complete analyses. The lowest recovery percentages occurred for field pH, conductivity and total  $H^+$  parameters. The same general pattern of data recovery emerges for the SES sampler, showing little differences between data recovery for the two types of samplers used during different times throughout the year. It should be noted that improved laboratory capabilities since 1981 have now placed conductivity and total  $H^+$  analyses near the top of the priority analyses list.

Table 2 shows a comparison of samples collected at pairs of sites located within 10 kilometers of each other. Three of the six pairs of sites had over 70% of all samples consistent (both sites collect a sample). The Railton/Whitman Creek pair had 62% consistent; and the Longwoods/Melbourne pair and Wellesley/North Easthope pair had 56.1% and 57.1% respectively. Whether these lower percentages of sample consistencies are due to spatial variabilities or operating problems is very difficult to ascertain.

## 2.2 Data Validation Observations

Data reported from the event precipitation network undergo a data validation process resulting in various office comments and analytical result remarks appended to the data. The following sections evaluate these comments and remarks as they pertain to the 1980-81 event precipitation data. Further details of these data validation procedures can be found in the report by Kirk (5).

As previously mentioned in Section 2.1.4. (Data Recovery), the SES sampler has been discontinued after April, 1982. The following section compares data between co-located SES and Aerochem Metrics samplers that led to the decision to operate the Aerochem Metrics sampler year round.

### 2.2.1 SES Sampler Bias

Co-located sampling using an Aerochem Metrics sampler and an SES sampler was initiated in 1981 at three sites in the event network, namely, Longwoods, Dorset, and Railton. The results of this study indicated a bias in collected data between the two types of samplers.

Higher concentrations of sulphates, nitrates, calcium, ammonia, magnesium, and higher pH measurements were usually observed in the SES type sampler. Figures 10 to 27 show these results in graphical form (magnesium results not shown). Longwoods showed a severe bias in pH measurements (figure 10) while Dorset pH measurements (figure 11) from the two collectors were very comparable. All three sites showed a bias in calcium results (figures 19-21), while none of the sites showed any bias in chloride results (figures 25-27).

In summarizing the remaining figures, the severity of the sampler bias was very much site dependent. Longwoods seemed to be much more susceptible to local dry contamination entering the bulk collector than the Dorset and Railton monitoring sites.

Sampling with SES samplers was discontinued during the winter sampling period. The Aerochem Metrics sampler is now the precipitation collector year-round at all event stations (effective November 1, 1982).

### 2.2.2 Sampler Efficiencies

At every event precipitation monitoring site, a precipitation depth is measured using either an Atmospheric Environment Service (AES) standard rain gauge (summer sampling) or a Nipher-shielded snow gauge (winter sampling). A sampling efficiency is calculated by converting the collected sample volume into an equivalent precipitation depth and comparing this equivalent depth with the measured gauge depth.

Figures 28 and 29 show the average sampling efficiency during 1981 for every monitoring site for both the Aerochem Metrics and SES samplers. Sampling efficiencies greater than 120% and any samples coded with a leak or spill have been excluded from these averages. All sites using the Aerochem Metrics collector, except Lac La Croix (only 3 samples), have sampling efficiency averages greater than 80%, ranging from 83.2% (Nithgrove) to 92.5% (Longwoods). Figure 30 shows a histogram of sampling efficiencies using the Aerochem Metrics sampler during 1981. Over 70% of all efficiencies occur in the sampler efficiency range of 70 to 110%.

Using the SES sampler, sampling efficiency averages ranged from 82.7% (Wellesley) to 93.5% (North Easthope). Quetico Centre's average efficiency of 80.1% is only based on 11 samples, while Lac La Croix's average efficiency of 101.3% is based on only 4 samples.

Average sampling efficiencies on a monthly basis (1981) for the SES sampler show that sampling efficiencies are highest during the months of November and April (104% and 106% respectively). This is not surprising since during both these months there were numerous rain events (rather than snow) which would result in an overcatch in the larger diameter SES sampler with respect to the smaller diameter Nipher-shielded snow gauge. Similarly, the lowest sampling efficiencies using the Aerochem Metrics sampler occurred during the months of May and October (82% and 81% respectively), reflecting the somewhat poorer collection characteristics during cooler temperatures.

Overall, sampling efficiency averages for the SES and Aerochem Metrics samplers were 88% (n = 428) and 89% (n = 640) respectively during the 1981 sampling period.

### 2.2.3 Sample Discrepancies

Screening procedures which are applied during data validation can result in office comment codes appended to the data. The following codes have been evaluated with respect to the 1980-81 event precipitation network:

- "C" - poor theoretical vs. observed conductivity comparison
- "J" - lab and field pH difference is large
- "L" - one or more parameters are high
- "M" - poor ionic balance

The office comment code L is subjectively appended to data if one or more parameters are high. The office comment codes C, J, and M are appended to data if calculated discrepancy percentages exceed upper or lower limits (97.5 and 2.5 percentiles respectively) based on cumulative frequency distributions of historical data. The upper and lower limits for these codes are:

$$\text{"C"} \left( \begin{matrix} +20\% \\ -20\% \end{matrix} \right) \text{ where } \% \text{ discrepancy} = \frac{(\text{Observed Conductance} - \text{Theoretical Conductance})}{(\text{Observed Conductance} + \text{Theoretical Conductance})} \times 200\%$$

$$\text{"J"} \left( \begin{matrix} +21\% \\ -3\% \end{matrix} \right) \text{ where } \% \text{ discrepancy} = \frac{(\text{Observed Lab pH} - \text{Observed Field pH})}{(\text{Observed Lab pH} + \text{Observed Field pH})} \times 200\%$$

$$\text{"M"} \left( \begin{matrix} -30\% \\ +10\% \end{matrix} \right) \text{ where } \% \text{ discrepancy} = \frac{(\text{Anion Equivalence} - \text{Cation Equivalence})}{(\text{Anion Equivalence} + \text{Cation Equivalence})} \times 200\%$$

Further details of the discrepancy calculations are found in the report by Kirk (5).

Conductivity, pH, and ionic balance discrepancies as well as samples with one or more parameters high have been tabulated in Table 3 for every monitoring site.

From Table 3 (Aerochem Metrics samples only), the Railton and Graham Lake monitoring sites (site numbers 10 and 12 respectively) had higher percentages of samples coded as having one or more parameters high than most sites (Railton 11.6%, Graham Lake 15.9%). However, using the SES sampler at these two sites, there were no samples with this coding.

The Whitman Creek site (number 9) had the highest percentage (14.3%) of samples with codings of one or more parameters high using the SES sampler. However, this site only had 6.2% of samples with this coding using the Aerochem Metrics sampler.

Generally, the frequency of appended validation codes using the two types of samplers does not show any significant siting problems. Only Longwoods (site number 2) consistently showed higher percentages of appended codes using both types of samplers, however, the frequency of these codes is not considered significant to indicate siting problems.

#### 2.2.4 Unreliable Results

Gross limit checks and the Dixon ratio test are used to identify outliers and unlikely results. These results are flagged in the data listings report with a "U" (unreliable) appended to the analytical result. The unreliable code is not to be interpreted as unreliable laboratory results. Rather, the code is used to identify any result that is suspicious and can be attributed to any component of the measurement system.

During the 1980-81 sampling period, 3.7% (352 out of 9,476) of all Aerochem Metrics analyses were coded "U" while 7.0% (554 out of 7,966) were coded "U" for all SES analyses.

Figure 31 shows the percentages of results labelled "U" for every site during 1980-81 using the Aerochem Metrics and SES samplers. All sites have fewer than 8% "U" results using the Aerochem Metrics sampler, with North Easthope (7.7%), Nithgrove (7.1%), and Whitman Creek (7.0%) recording the highest percentages. Using the SES sampler, Longwoods (12.2%) and Wellesley (12.8%) recorded the highest percentage of "U" data.

Figure 32 shows the average percentage of SES sampler results coded "U" on a regional basis. The Southwestern region, which is predominantly an agricultural area, had the highest percentage namely 11.3%; while the Northwestern region's average percentage was the lowest (0.3%)

#### 2.2.5 Non-Standard Collection Periods

Samples that have been collected over a period longer than 24 hours (multi-day samples) are coded "Z" in the data report. Table 4 shows the percentage of samples with this coding for every site. Dorset recorded the highest percentage, namely 6.5%. The majority of these multi-day samples from Dorset occurred during weekend sample collection periods. Overall, the entire network had an average of 2.3% ( 46 out of 2,034).



### 3.0 AIR SAMPLING NETWORK

The following sections assess the performance of the daily air sampling network during the 1980-81 sampling period. Both field and data validation observations are used for this evaluation.

#### 3.1 Field Observations

Field observations are appended by the operator or environmental technician responsible for the operation of the site. These observations include sampler malfunctions, hydro failures, filter pack leaks, and suspected or known contamination of the filter packs in the field. Table 5 shows the percentages of these codes appended to samples for every monitoring site.

##### 3.1.1 Sampler Malfunctions

Sampler malfunctions are coded as an "A" in the data listing report. From Table 5, site malfunction percentages were: Charleston Lake 0.7%, Dorset 1.5%, Longwoods 1.7%, and Fernberg 8.6%. Overall, out of 1,136 samples submitted for analyses, 21 were coded as having a sampler malfunction (1.8%).

The most common malfunction of the daily air sampler is the failure of the sequencing mechanism circuit. To reduce the length of down-time at the Fernberg site (located in Minnesota) a spare air sampler has been made available to the regional technician.

##### 3.1.2 Hydro Failures

All sites but Dorset (5.4%) had less than 1% of samples coded as having hydro failures occur during the 1980-81 sampling period (Table 5). The majority of these hydro failures at Dorset (85%) occurred shortly after the initial installation in 1980. During 1981, only 1.2% (4 of 324) of all samples were coded as having hydro failure occurrence. Of these 4 samples, no total volumes were less than 23,000 litres; indicating that hydro was restored within a few hours.



### 3.1.3 Suspected Filter Pack Leaks or Flow Line Problems

Suspected filter pack leaks and flow line problems are coded "E" and "G" respectively. Suspected filter pack leaks are usually coded when the filters are observed to be mis-aligned or crinkled upon unloading. The percentage of samples coded with this condition (Table 5) ranged from 0.3% (Longwoods) to 9.9% (Fernberg). Other site percentages were Charleston Lake 0.4%, and Dorset 3.8%.

Upon checking the associated field submission sheets for the Fernberg site with this coding (8 out of 81 samples), it was found that these 8 samples were consecutive samples collected during the last week of October 1981. No additional explanation was provided on the submission sheets to account for these codings except that many of these samples did have low total flow volumes. During this time period, samples were shipped directly to Toronto from Fernberg bypassing the regional technician. As well, October 1981 was the first month of operation at this site. From all available information, the code E should be removed from these 8 samples and replaced by the flow line problem code (G).

Flow line problems (coded G) were coded 0% at Dorset, 0.4% at Charleston Lake, 1.4% at Longwoods, and 8.6% at Fernberg. Again, all the "G" codes entered as field comments at Fernberg should not have been appended to the data. Sampler malfunctions were coded for these samples, therefore the "G" code should not have been appended.

Field comment codes have subsequently been evaluated and modified to eliminate redundancy. Field comment codes such as "known or suspected filter pack leak", and "flow line problems" have been replaced with more clearly defined codes such as "filter placement incorrect" and "flow volume suspect (state reason)".

#### 3.1.4 Known or Suspected Contamination

Samples are coded an "H" (known contamination) if a filter pack drops on the ground, or if a filter drops on the floor, etc. Samples are coded an "I" if a filter pack is suspected of contamination.

Dorset had 8.5% of all samples coded as either known or suspected contamination while Longwoods had 5.5%, Charleston Lake 1.1%, and Fernberg 0% (Table 5). Overall, 60 out of 1,136 samples were coded as known or suspected contamination in the field (5.3%).

A further investigation of the field submission sheets at Dorset revealed a number of incidents that could account for the higher frequency of these codes. On-site construction, helicopter activity nearby, and repairs to the filter pack shelter housing were some of the activities that resulted in suspected contamination codes appended to consecutive filter packs loaded on the tower. Data flagged as "U" from Dorset (discussed in section 3.2.2) does not coincide with any of the data appended with known or suspected contamination codes.

Similarly, samples from Longwoods and Charleston Lake coded with the field comment "suspected or known contamination" never resulted in any results flagged "U" after data validation techniques. The present field submission sheet has incorporated the two codes "H" and "I" together under one code indicating that contamination may have been introduced in the field.

#### 3.2 Data Validation Observations

Data validation can result in a number of office comment and result remark codes appended to the data. The following sections evaluate the frequency of these observations. Further details of data validation can be found in the report by Kirk (6).

### 3.2.1 Data Recovery

Figure 33 shows the data recovery percentages for all sites during 1980-81. The data recovery calculation is based upon the number of missing data and data coded "U" (discussed below). Using missing data only, all monitoring sites have over 85% data recovery. Using both missing and data coded "U" all sites have over 83% data recovery. Overall, the air sampling network had 92.1% data recovery when calculated using missing and unreliable data.

### 3.2.2 Unreliable Results

As discussed in the event precipitation network section, the result code "U" is appended to data during validation procedures if the data is suspicious (gross limit checks and principal component analysis). Further details of the validation procedures for air monitoring data are available in a separate document (5).

Table 6 shows the percentage of results coded "U" at each site. All sites have no greater than 5% data coded "U", and combining all sites, 2.2% (123 out of 5,680 sample results) of all data was coded "U".

Table 7 provides the percentage of data coded "U" by parameter type. Except on two occasions "U" codings, once applied, were appended to all parameters of a sample. Therefore, the percentage of unreliable data by parameter type is evenly distributed.

### 3.2.3 Passive Filter Pack Results.

To correct for passive filter pack loadings, one filter pack is left passive on the sampling tower (without drawing air through) for a 1 week period to correspond with the active filter packs. Table 8 shows the geometric means of passive filter pack loadings for all sites during 1981. The geometric means are reported as micrograms per filter.

Fernberg recorded the highest geometric mean of  $\text{SO}_2$  passive loadings, 19.1 ug/filter; while other sites had loadings between 4 and 8 ug/filter. The geometric mean for Fernberg, however, is only based on 13 sample results from October to December (due to a later start-up date) and since  $\text{SO}_2$  loadings are usually highest during the winter-time, the geometric mean for Fernberg during 1981 is not a representative average.

Geometric means for passive samples have been calculated from the 1982 data in Table 9. Again Fernberg recorded the highest mean passive  $\text{SO}_2$  loading of 21.9 ug/filter compared to 18.1, 14.9 and 12.5 ug/filter for Longwoods, Charleston Lake, and Dorset respectively. Since the Fernberg site is remotely located in northern Minnesota, no explanation is presently known for the higher  $\text{SO}_2$  passive loadings.

The 1981 and 1982 geometric means of passive loadings of other parameters are consistent in terms of site location and distance from emission sources. For  $\text{SO}_4^{=}$ , the 1982 geometric means for passive samples were 1.16, 1.10, 1.04 and .89 ug/filter for Longwoods, Charleston Lake, Dorset, and Fernberg respectively. Longwoods is the southernmost site with respect to emission sources followed by Charleston Lake, Dorset, and Fernberg. The same pattern generally emerges for  $\text{NO}_3^-$ ,  $\text{HNO}_3$ , and  $\text{NH}_4^+$  passive loadings.

Comparing 1981 to the 1982 passive loadings, the geometric means are comparable except for  $\text{SO}_2$  and  $\text{NO}_3^-$ . The passive loading geometric means increased, on average, by a factor of 2 for these two parameters.

#### 3.2.4 Air Volumes

Air volumes in the daily air sampling network are determined by temperature compensated dry gas meters connected to digital volume counters. Figure 34 is a frequency histogram of total air volumes for all sites combined. The 50th percentile corresponds to a total air volume of just over 26,000 litres. This volume represents an average flow rate of approximately 18 litres per minute (lpm). While network documentation and procedures state that sampling flow rates are to be set at 25 lpm, most of the daily air sampling instruments cannot maintain this high flow rate with loaded filter packs located at a height of 10 metres. Almost all samples (98.5%) have average flow rates less than 23 lpm.

Table 10 shows the average air volume of samples collected at each site. All sites but Fernberg have average air volumes of approximately 27,000 litres. Fernberg's average air volume was approximately 22,000 litres. Because of these lower volumes, Fernberg had a higher percentage of invalidated data, namely 2.5% (Table 10). Invalidated data are identified by the code "F" in the data listings report, and is appended whenever the total air volume is less than 10,000 litres. Combining all sites, 2.1% of all samples were invalidated due to insufficient air volumes.

It should be noted that the Fernberg site is not located near the regional office as in other regions. All daily air sampling sites except Fernberg are less than a 2 hour drive from the regional offices with the regional technicians responsible for the operation and collection of samples at the sites.

During the initial sampling periods at Fernberg, samples were shipped directly from operators located near the site to the office located in Toronto. This arrangement resulted in sample shipment delays to and from the site due to logistical problems (customs, brokers, etc.). Presently, the regional technician in the Northwestern region visits the site on a monthly basis with operators located on-site to carry out filter pack changing. Because of this type of arrangement, instrument problems may not be identified as quickly and repairs cannot be carried out as quickly as other sites where regional technicians are visiting the site every week. To improve operations, a spare sampler is now kept on-site to reduce instrument downtime.

### 3.3. Site Concentration Comparisons

Site concentration comparisons of geometric means (1981) for every parameter are shown in Figures 35 to 37. Longwoods was found to have the highest mean concentration of every parameter followed by Charleston Lake, Dorset, and Fernberg. This pattern is expected since Longwoods is the most southernmost site and Fernberg the northernmost site with respect to emission sources. The largest relative difference in geometric means among these sites occurred for nitrates. Longwood's geometric mean was  $0.26 \text{ ug/m}^3$  compared to 0.07, 0.06, 0.02 for Charleston Lake, Fernberg, and Dorset respectively.

#### 4.0 LABORATORY QUALITY CONTROL DATA

Samples collected in the daily precipitation and air sampling networks are analyzed in the Water Quality Section at the Ministry of the Environment laboratory located on Resources Road in Toronto. The following section summarizes the precision and accuracy of the Water Quality Section based on a minimum of three month's quality control data during 1980 (7). The results apply to both the precipitation samples and the aqueous extracts of the air filter samples.

##### 4.1 Precision and Accuracy

Calibrations were carried out by using standardized solutions covering the range of instrument response. Calibrations are confirmed by using two quality control standards (QC-A and QC-B) which are made up and maintained independently of the calibration standards. The accuracy of laboratory measurements are represented by the percentage differences between the theoretical concentrations of the control standards and the mean concentrations found after calibrations.

Table 11 provides a list of water quality parameters and the accuracies obtained using the control standards. To control both the blank and slope bias during calibration, the control concentrations of QC-A and QC-B are chosen to be approximately 70% and 10% of full scale respectively.

Precision in the Water Quality Section (within-run repeatability) is represented by the standard deviations of the differences observed between within-run duplicate analysis of routine samples. Table 12 lists all water quality parameters and the standard deviations of the differences of duplicate results. The observed differences in duplicate results were accumulated and sorted according to three concentration ranges, namely: 0-20%, 20-50%, and 50-100% of full scale. A standard deviation was then calculated for each of these three concentration ranges. Only concentration ranges of 0-20% and 20-50% full scale are presented in Table 12 since the majority of sample results lie within these two ranges.

Table 13 summarizes the accuracy and precision of the Water Quality Section during the three month period in 1980. The concentration ranges in Tables 11 and 12 which most closely represented field sample concentrations were used to calculate precision and accuracy estimates in Table 13. The accuracy of every water quality parameter is expressed as a  $\pm$  percentage (extracted from Table 11) using the following expression:

$$\left| \frac{\text{Theoretical Conc.} - \text{Observed Conc.}}{\text{Theoretical Concentration}} \right| \times 100$$

The precision of every parameter is extracted from Table 12 and is expressed using the coefficient of variation:

$$\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$$

It should be noted that percentage differences of small concentrations may be misleading. For example, a percentage error of  $\pm 30\%$  using a concentration of 0.08 mg/l converts to an error of  $\pm 0.02$  which corresponds to an interval of 0.06 to 0.10. Therefore, the concentration level must always be kept in mind when interpreting accuracies and precision. Percentages have been introduced since future field QC data, where poorer precision and accuracy estimates are expected, will be expressed as  $\pm$  percentages.

From Table 13, all water quality parameters except for conductivity ( $\pm 11\%$ ), had accuracies within  $\pm 10\%$ . Precision estimates varied with parameter type. Acid-based related parameters (total  $\text{H}^+$ , sulphate, nitrate and ammonium) had precisions within  $\pm 5\%$ . All other parameters except potassium ( $\pm 15\%$ ) and sodium ( $\pm 10\%$ ) had precisions less than  $\pm 10\%$ .



## 5.0 SUMMARY

The following sections summarize the performance assessment of the daily precipitation and air sampling networks. Actions to be taken as a result of this assessment are provided as well.

### 5.1 Precipitation Sampling Network (1980-81)

1. A total of 2,034 samples were collected from 16 monitoring sites.
2. 5.7% of all samples had sampler malfunction codings.
3. 3.7% of all samples leaked or spilled.
4. Less than 1% of all samples were lost, and 5.4% of all samples were not submitted.
5. Data recovery averaged 73%.
6. Higher concentrations of sulphates, nitrates, calcium, ammonium, magnesium, and higher pH values were observed in some samples collected using the SES sampler compared to using the Aerochem Metrics sampler. The concentration differences between these two samplers were very site dependent with the Longwoods site much more susceptible to local dry contamination entering the SES (bulk) sampler.
7. The average collection efficiency of the SES sampler and Aerochem Metrics sampler was 88% and 89% respectively during 1981.
8. Conductance, pH, and ionic balance irregularities occurred in 4.1%, 1.8% and 3.3% respectively in all Aerochem Metrics sample analyses. Using the SES sampler, conductance, pH, and ionic balance irregularities occurred in 4.2%, 1.3%, and 4.4% of all sample analyses respectively.



9. 3.7% of all sample results collected in the Aerochem Metrics sampler were coded unreliable, while 7.0% of all SES samples were coded unreliable.
10. Non-standard collection periods were coded in 2.3% of all samples.
11. Laboratory analyses during 1980-81 are estimated to be accurate within  $\pm 11\%$ . Precision varies with parameter type but total  $H^+$ , sulphate, nitrate, and ammonium were all within  $\pm 5\%$ .

The daily precipitation monitoring network has undergone changes since its inception in 1980. SES samplers were discontinued after April, 1982 because of the susceptibility of the sampler to dry deposition. A modified sensor head was installed in the Aerochem Metrics sampler in the fall of 1984 to improve the sensing characteristics during snow type events. Co-located samplers have been installed as part of a comprehensive quality assurance program to estimate overall sampling precision.

Based on the assessment of the 1980-81 data, the following actions are to be taken:

1. Replace the Whitman Creek site with a site that has access to A.C. power.
2. Evaluate the change in data recovery due to the year-round use of the Aerochem Metrics sampler.
3. Regional technicians are to pay close attention to inconsistent sample collection dates and sample volumes between sites. Daily precipitation site summary sheets should be promptly filled out and evaluated to determine any site or field data inconsistencies.

## 5.2 Air Sampling Network (1980-81)

The following points summarize the performance of the daily air sampling network during 1980-81:

1. A total of 1,136 samples (active filter packs) were collected from 4 monitoring sites.
2. 1.8% of all samples had sampler malfunction codings.
3. 5.3% of all samples were coded by technicians as being possibly contaminated. No samples with this coding resulted in any data being validated as unreliable.
4. Data recovery averaged 92.1% (calculated using missing and unreliable data).
5. 2.2% of all samples were coded as unreliable.
6. 98.5% of all samples had flow rate averages of less than 23 litres per minute. The average flow rate (median) of all samples was 18 litres per minute.
7. 2.1% of all samples were invalidated due to insufficient air volumes.
8. For all parameters, the Longwoods monitoring site had the highest geometric mean concentrations followed by Charleston Lake, Dorset, and Fernberg.
9. Water quality analyses had laboratory accuracy and precision estimates within  $\pm 5\%$  for aqueous filter extracts.

Based on the assessment of the 1980-81 daily air sampling data, the following actions are to be taken:

1. Regional technicians are to carry out preventive maintenance as outlined in the technical and operating manual in order to reduce instrument downtime (while the 1980-81 downtime is quite acceptable, it is expected that preventive maintenance will become increasingly important).
2. Identify the critical components that commonly fail in the sequential air sampler and replace them on a routine basis.
3. Field comment code guidelines are to be documented to ensure that these codes are applied uniformly across the network.
4. Investigate SO<sub>2</sub> passive loadings from the Fernberg site in order to account for the unexpectedly high passive values.
5. Sequential air samplers are to be replaced and repaired whenever the sampling flow rate drops under 17 litres per minute.

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**Table 1.**  
Data Recovery - Daily Precipitation Network 1980-81

<u>Parameter</u>	<u>Data Recovery %</u>	
	Aerochem Metrics (n = 1,138)	SES (n = 896)
Conductivity	52.0	56.7
Field pH	32.9	36.9
Lab pH	85.1	73.3
Total H <sup>+</sup> (pH 8.3)	52.1	53.8
Sulphate	82.3	83.1
Nitrate (as N)	82.8	84.3
Calcium	67.2	62.5
Magnesium	66.8	62.7
Chloride	82.2	80.6
Potassium	67.9	69.9
Sodium	66.6	68.2
Ammonium (as N)	70.9	70.6

Note: Data recoveries calculated by excluding reported results flagged as "U", unreliable

**Table 2.**  
Comparison of Samples Collected  
Daily Precipitation Network 1980-81

Site	Period	Samples Collected	# Samples Inconsistent	# Samples Consistent	% Samples Consistent
Longwoods	May 9-Nov. 22/81	63	19	46	56.1
Melbourne		65	17		
Wellesley	May 7 - Nov. 27/81	66	25	52	57.1
North Easthope		77	14		
Raven Lake	May 5 - Oct. 28/81	60	3	57	90.5
Balsam Lake		60	3		
Nithgrove	May 5 - Oct. 24/81	56	10	49	74.2
Dorset		59	7		
Railton	Oct. 24 - Nov. 14/80	68	14	51	62.2
Whitman Creek	and May 5 - Oct. 28/81	65	17		
Charleston Lake	May 5 - Oct. 28/81	88	6	69	73.4
Graham Lake		75	19		
<b>Overall</b>		802	154	324	68.8%

Note: % Samples Consistent is defined as:  $\frac{\# \text{ samples consistent} \times 100}{\# \text{ samples consistent} + \# \text{ samples inconsistent}}$

**Table 3.**  
Sample Discrepancies - Aerochem Metrics and SES Sampler

Site No.	# Samples		% Conductivity		% ΔpH High		% Ionic Balance		% ≥ 1 Parameter High	
	Aero	SES	Aero	SES	Aero	SES	Aero	SES	Aero	SES
1	94	47	3.2	6.4	1.1	2.1	0	6.4	5.3	2.1
2	130	67	6.2	13.4	3.1	1.5	1.5	10.4	0.8	4.5
3	125	96	5.6	4.2	0	0	6.4	7.3	5.6	7.3
4	67	63	3.0	1.6	0	0	1.5	1.6	0	3.2
5	61	63	3.3	3.2	0	0	0	1.6	0	0
6	83	52	4.8	3.8	1.2	0	8.4	5.8	3.6	0
7	56	73	0	1.4	0	0	5.4	1.4	0	2.7
8	133	84	3.0	2.4	0	0	5.3	3.6	8.3	6.0
9	65	63	0	6.3	3.1	3.2	3.1	6.3	6.2	14.3
10	121	52	6.6	0	6.6	5.8	3.3	0	11.6	0
11	88	80	1.1	3.8	2.3	3.8	0	3.8	0	8.8
12	107	55	6.5	5.5	1.9	3.6	2.8	3.6	15.9	0
13	5	39	0	2.6	20.0	0	0	2.6	0	0
14	-	29	-	3.4	-	0	-	0	-	0
15	3	6	33.3	0	0	0	33.3	0	0	0
16	-	27	-	7.4	-	0	-	11.1	-	0

Aero - Aerochem Metrics Sampler

SES - Sudbury Environmental Study Sampler

**Table 4.**  
Non-Standard Collection Periods  
Daily Precipitation Network 1980-81

<u>Site No.</u>	<u># Samples Collected</u>	<u>% Samples Coded "Z"</u>
1	141	0
2	197	3.2
3	221	0.5
4	130	1.5
5	124	1.6
6	135	0
7	129	0.8
8	217	6.5
9	128	0
10	173	6.4
11	168	0
12	162	5.6
13	44	2.3
14	29	0
15	9	0
16	27	0

**Overall: 2.3%**



**Table 5.**

**Field Observations - Daily Air Sampling Network  
1980-81**

Site	# Samples Collected	% Sampler Malfunctions	% Known/Suspected Hydro Failures	% Suspected Filter Pack Leak	% Flow Line Problems	% Known/Suspected Contamination
Longwoods	291	1.7	0.3	0.3	1.4	5.5
Dorset	480	1.5	5.4	3.8	0	8.5
Charleston Lake	284	0.7	0.4	0.4	0.4	1.1
Fernberg	81	8.6	0	9.9	8.6	0
<b>Overall</b>	1136	1.8	2.5	2.5	1.1	5.3

**Table 6.**  
 Unreliable Data - Daily Air Sampling Network  
 1980-81

<u>Site</u>	<u># Samples Collected</u>	<u>% Data Coded Unreliable</u>
Longwoods	291	2.8
Dorset	480	2.1
Charleston Lake	284	1.1
Fernberg	81	4.2
<b>Overall</b>	<b>1,136</b>	<b>2.2%</b>

**Table 7.**  
 Unreliable Data Distribution Vs. Parameter Type  
 Daily Air Sampling Network 1980-81

<u>Parameter</u>	<u># Coded Unreliable</u>	<u>% Unreliable Results</u>
SO <sub>2</sub>	26	.46
SO <sub>4</sub> <sup>=</sup>	25	.44
HNO <sub>3</sub>	24	.42
NH <sub>4</sub> <sup>+</sup>	24	.42
NO <sub>3</sub> <sup>-</sup>	24	.42

**Table 8.**  
Passive Loading - 1981  
Daily Air Sampling Network

Geometric Means - ug/filter

Site	n	SO <sub>2</sub>	n	SO <sub>4</sub> <sup>=</sup>	n	Nitric Acid (as N)	n	Ammonium (as N)	n	Nitrate (as N)
Longwoods	44	8.5	44	1.39	44	1.77	44	.161	44	.44
Dorset	43	5.3	51	1.15	52	1.34	52	.084	51	.27
Charleston Lake	40	5.2	41	1.01	41	1.08	37	.128	41	.30
Fernberg	13	19.1	13	.72	13	.70	12	.116	13	.29

20 x 60 x 2.4 ~ 30 m<sup>3</sup> d<sup>-1</sup>  
1980

**Table 9.**  
Weekly Passive Loadings - 1982  
Daily Air Sampling Network

Geometric Means - ug/filter

Site	n	SO <sub>2</sub>	n	SO <sub>4</sub> <sup>=</sup>	n	Nitric Acid (as N)	n	Ammonium (as N)	n	Nitrate (as N)
Longwoods	48	18.1	50	1.16	50	2.10	50	.190	50	.51
Dorset	51	12.5	51	1.04	51	1.08	51	.101	51	.66
Charleston Lake	51	14.9	51	1.10	51	1.34	51	.108	51	.69
Fernberg	47	21.9	47	.89	47	.66	47	.088	47	.61

**Table 10.**  
Air Volumes and Data Invalidated Vs. Site  
Air Sampling Network 1980-81

<u>Site</u>	<u>Average Air Volume</u>	<u>% Data Invalidated (due to air volume &lt; 10,000 litres)</u>
Longwoods	27,337	1.7
Dorset	27,230	1.7
Charleston Lake	26,648	0.4
Fernberg	21,776	2.5

Table 11.

Laboratory Accuracy - Water Quality Parameters

Parameter	Units	Calibration Range	Resolution*	Quality Control Standard - A				Quality Control Standard - B			
				n	Theoretical Concentration	Mean Concentration Found	Percentage Difference	n	Theoretical Concentration	Mean Concentration Found	Percentage Difference
Conductivity	us/cm	0-100	1.5	54	73.9	73.8	0.1	54	14.9	16.5	10.7
pH	pH units	3.50 - 7.00	0.001	110	6.86	6.95	1.3	108	4.01	4.01	0
Total H+ (pH 8.3)	mg/l	0.2	0.0001	57	0.500	0.501	0.2	56	0.200	0.219	9.5
Sulphate	mg/l	0.07 - 10.0	0.1	177	8.00	7.99	0.1	177	2.00	2.02	1.0
Nitrate (N)	mg/l	0.02 - 2.00	0.02	167	1.60	1.60	0	165	0.40	0.40	0
Calcium	mg/l	0.02 - 2.00	0.02	36	1.20	1.22	1.7	36	0.20	0.20	0
Chloride	mg/l	0.03 - 1.50	0.02	138	1.20	1.20	0	138	0.30	0.30	0
Magnesium	mg/l	0.01 - 0.50	0.005	21	0.300	0.294	2.0	21	0.050	0.047	6.0
Potassium	mg/l	0.02 - 1.00	0.01	21	0.600	0.603	0.5	21	0.100	0.097	3.0
Sodium	mg/l	0.01 - 1.00	0.01	36	0.600	0.600	0	37	0.100	0.098	2.0
Ammonium	mg/l	0.006 - 0.400	0.004	92	0.300	0.301	0.3	93	0.100	0.106	6.0

\* Resolution is arbitrarily based on the readability of  $\pm 1$  line on a 100 line strip chart recorder (1% of full scale). In most cases, analysts can read to better than 1%.

**Table 12.****Laboratory Precision (within-run) - Water Quality Parameters**

Parameter	Units	Concentration Range 0-20 % F.S.				Concentration Range 20-50% F.S.			
		n	Mean	Standard Deviation	Coefficient of Variation %	n	Mean	Standard Deviation	Coefficient of Variation %
Conductivity	us/cm	14	10.5	0.3	3	44	35.5	0.4	1
pH	pH units	0	-	-	-	3	4.37	0.023	-
Total H+ (pH 8.3)	mg/l	1	0.023	-	-	4	0.0814	0.00018	<1
Sulphate	mg/l	15	1.16	0.04	3	31	3.10	0.108	3
Nitrate (asN)	mg/l	12	0.25	0.01	4	19	0.70	0.016	2
Calcium	mg/l	25	0.187	0.011	6	10	0.690	0.026	4
Chloride	mg/l	17	0.160	0.015	9	9	0.501	0.013	3
Magnesium	mg/l	10	0.056	0.003	5	6	0.186	0.002	1
Potassium	mg/l	16	0.079	0.012	15	3	0.340	0.015	4
Sodium	mg/l	29	0.071	0.007	10	9	0.286	0.013	5
Ammonium (asN)	mg/l	-	-	-	-	3	0.742	0.010	1



**Table 13.**

**Accuracy and Precision Summary**  
**Water Quality Parameters**

Parameter	Units	Accuracy		Precision	
		Concentration	± %	Concentration	± %
Conductivity	us/cm	15	11	10	3
pH	pH units	4.0	-	4.4	-
Total H+ (pH 8.3)	mg/l	0.2	10	0.1	1
Sulphate	mg/l	2.0	1	3.1	3
Nitrate (asN)	mg/l	0.4	1	0.3	4
Calcium	mg/l	0.2	1	0.2	6
Chloride	mg/l	0.3	1	0.2	9
Magnesium	mg/l	0.05	6	0.06	5
Potassium	mg/l	0.1	3	0.08	15
Sodium	mg/l	0.1	2	0.1	10
Ammonium (asN)	mg/l	0.3	1	0.7	1

Fig.1 Site Map  
Daily Precipitation Monitoring Network

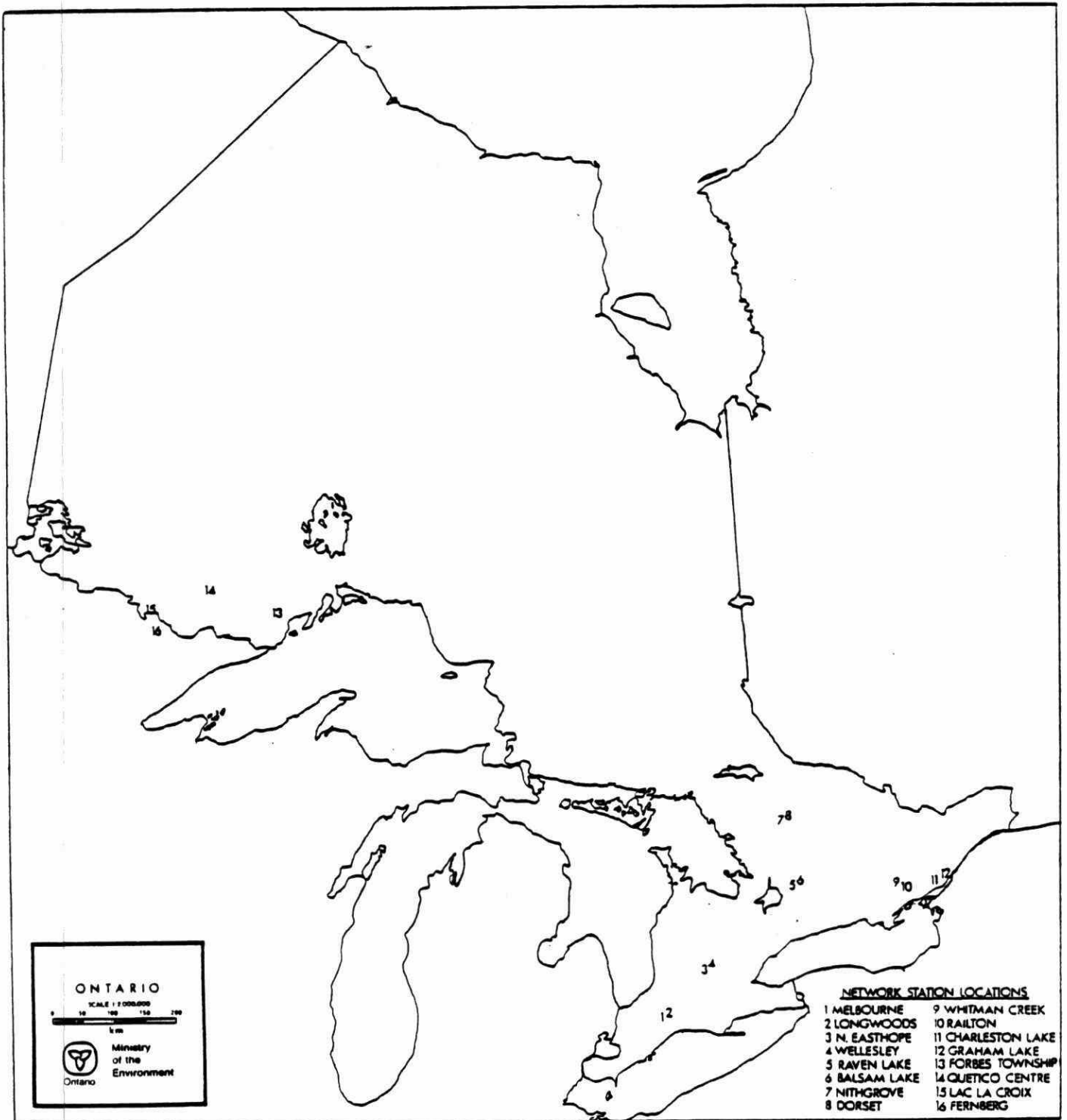
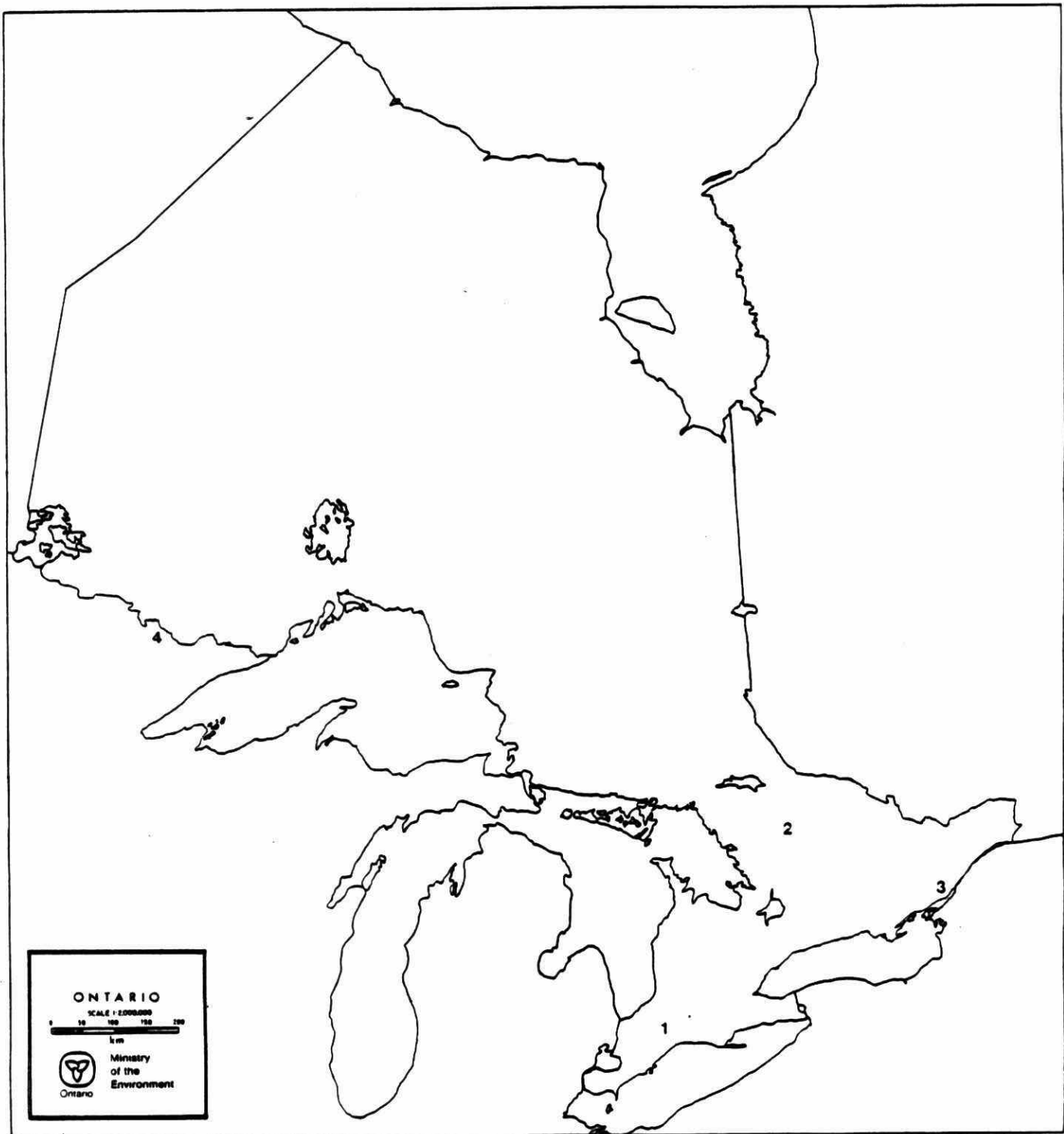


Fig. 2 Site Map  
Daily Air Sampling Network



MAP REF. NUMBER	STATION NAME	MOE REGION	ELEVATION (m)	LATITUDE NORTH	LONGITUDE WEST	UTM COORDINATES	
						NORTHING	EASTING
01	Longwoods	Southwestern	239	42°53'	81°29'	4747850	460700
02	Dorset	Central	320	45°13'	78°56'	5009600	662450
03	Charleston Lake	Southeastern	92	44°30'	76°03'	4927500	417150
04	Fernberg	Northwestern	506	47°50'	91°52'	5316000	585000

Fig. 3 Sampler Malfunctions - Aerochem Metrics Sampler  
1980-81

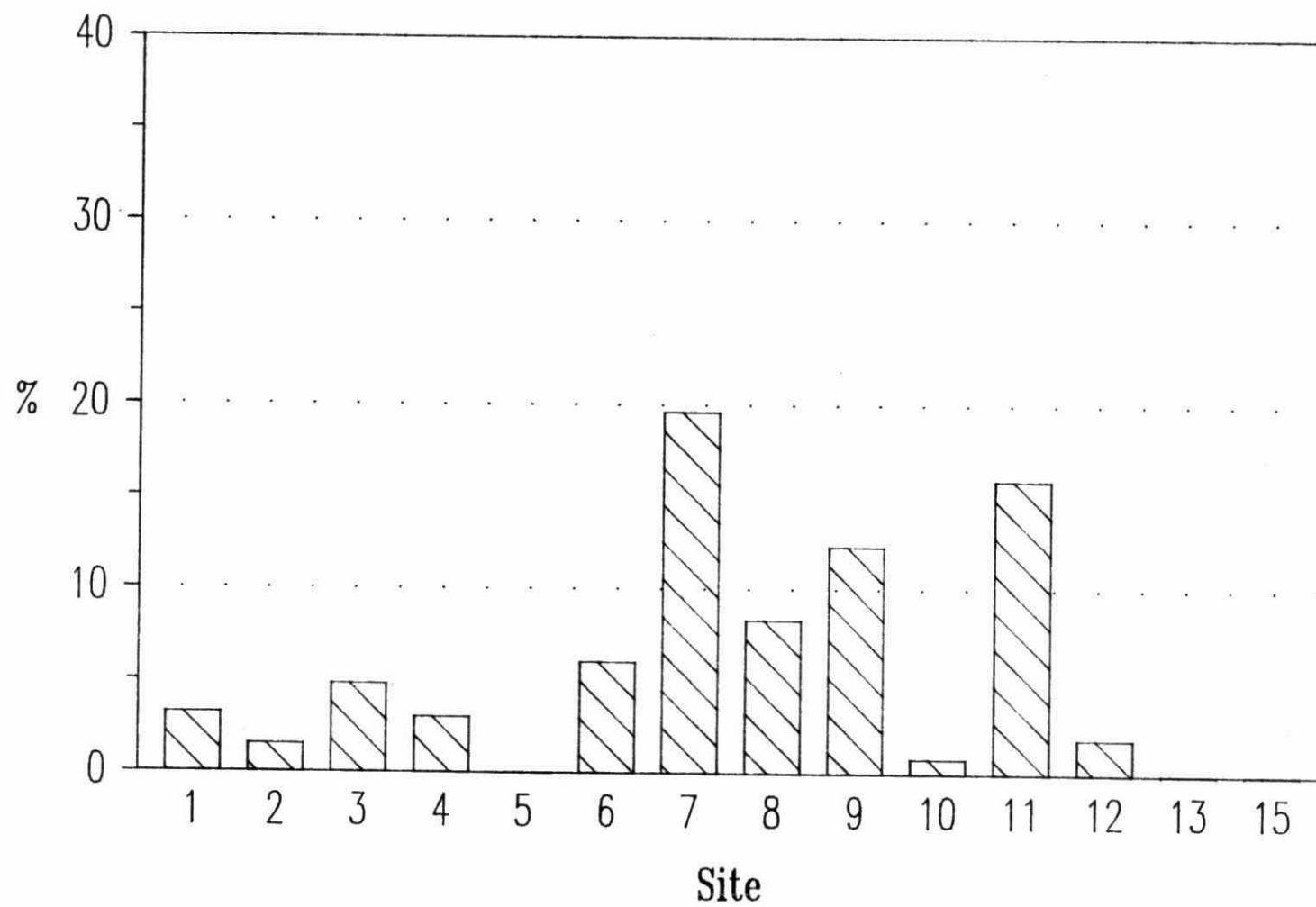


Fig. 4 Sampler Malfunctions Vs. Month  
Aerochem Metrics 1981

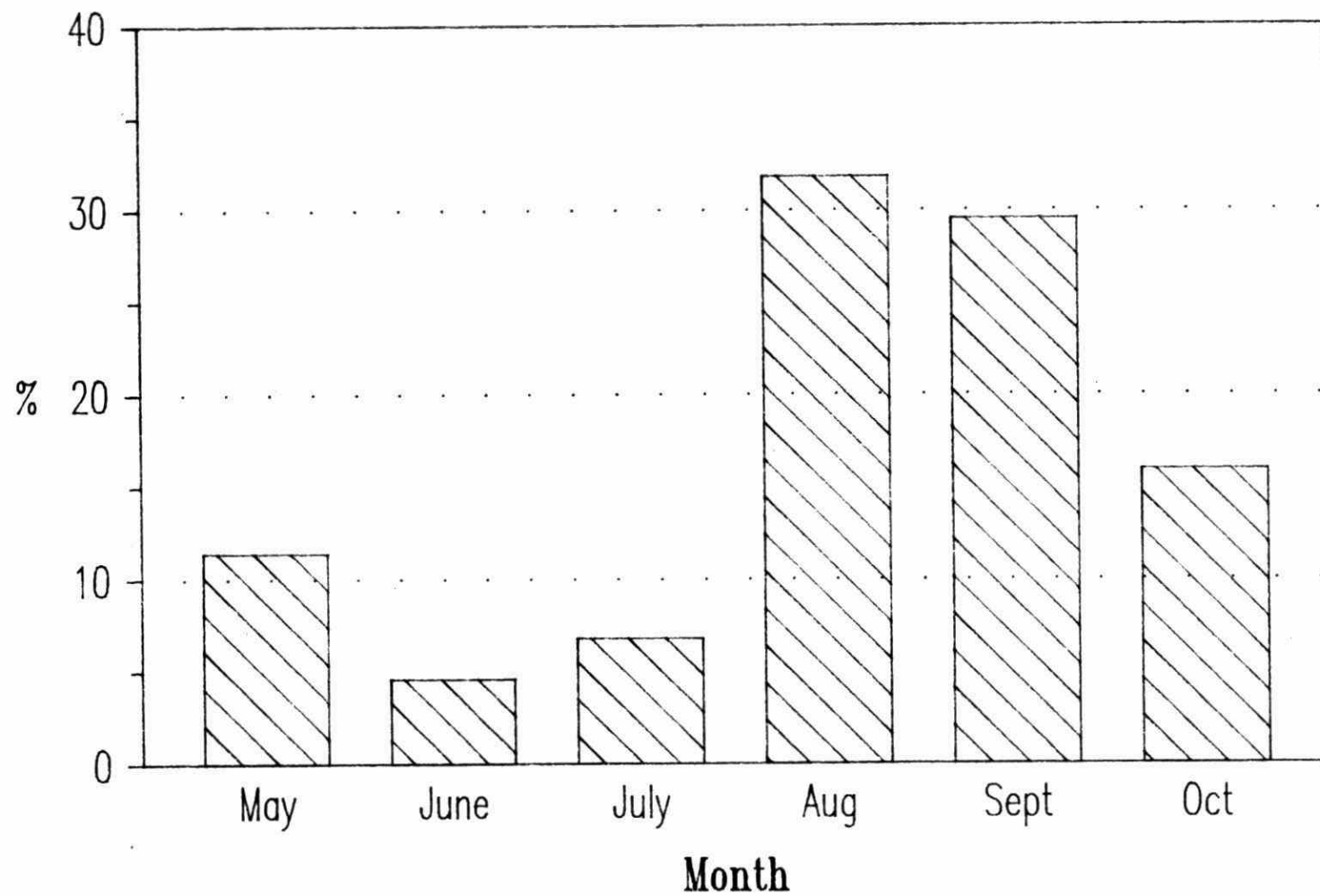


Fig. 5 Sample Leaks/Spills – Daily Precip. Network  
1980-81

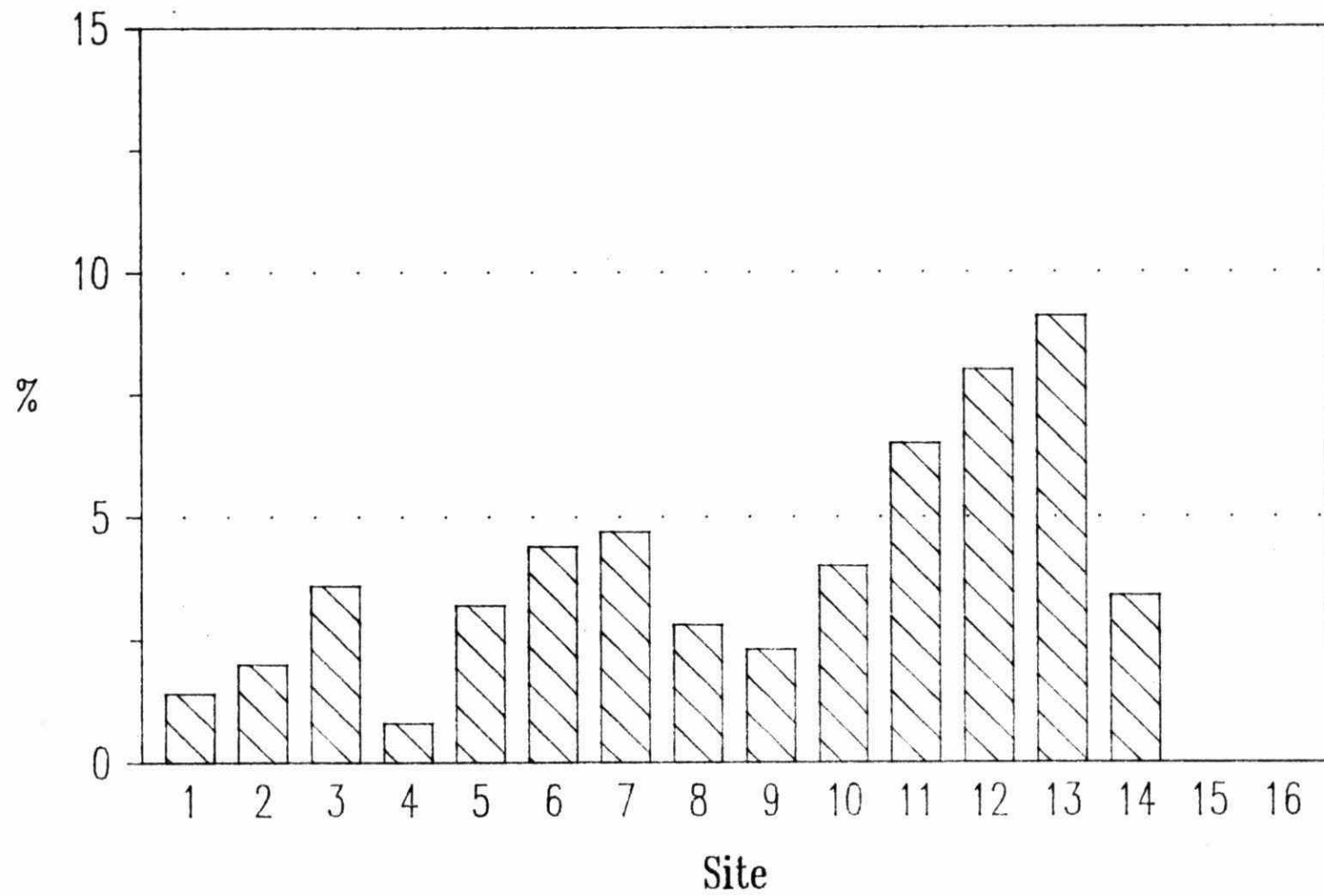


Fig. 6 Sample Leaks/Spills Vs. Month  
Daily & Monthly Precip. Networks 1981

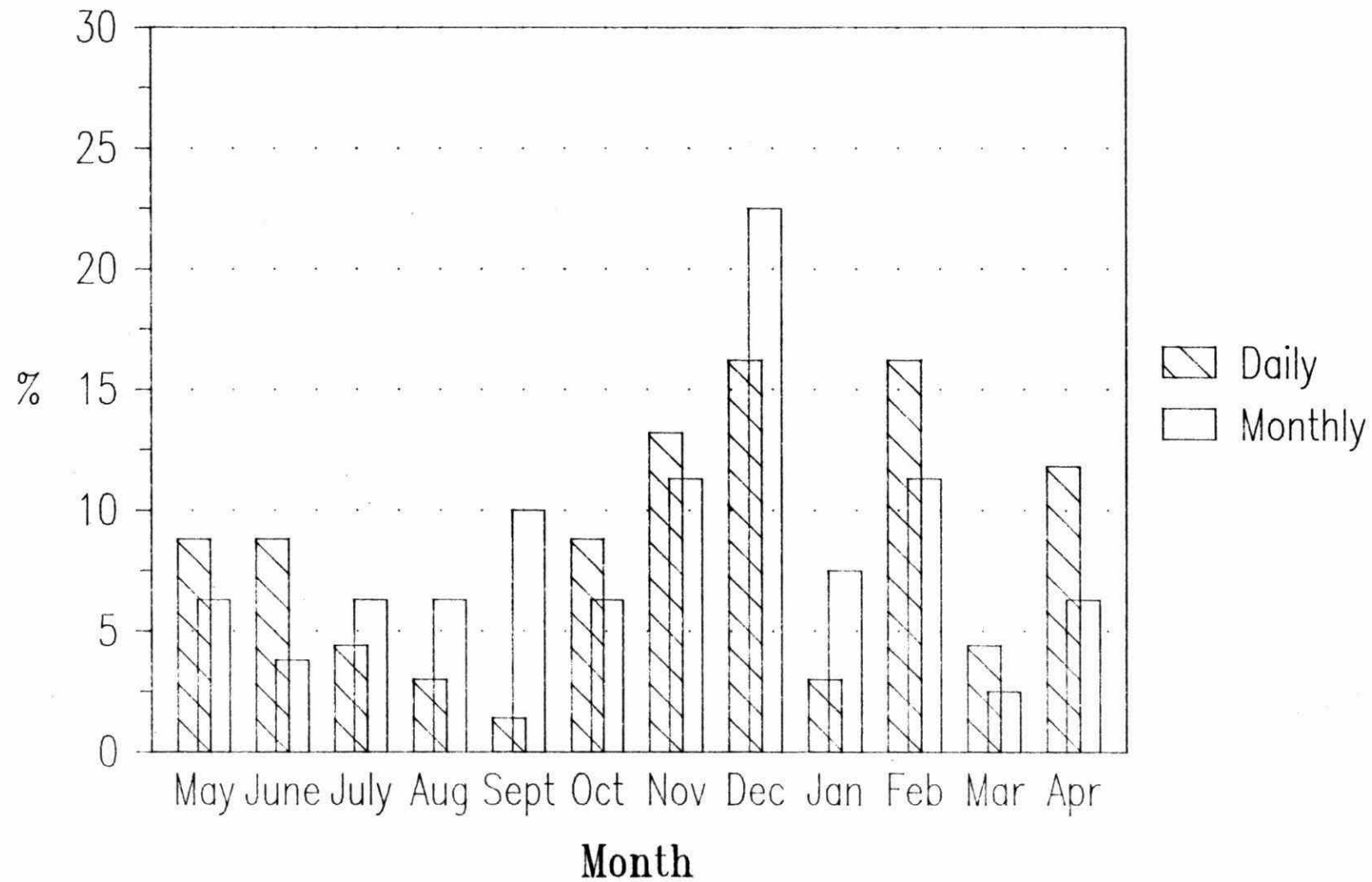
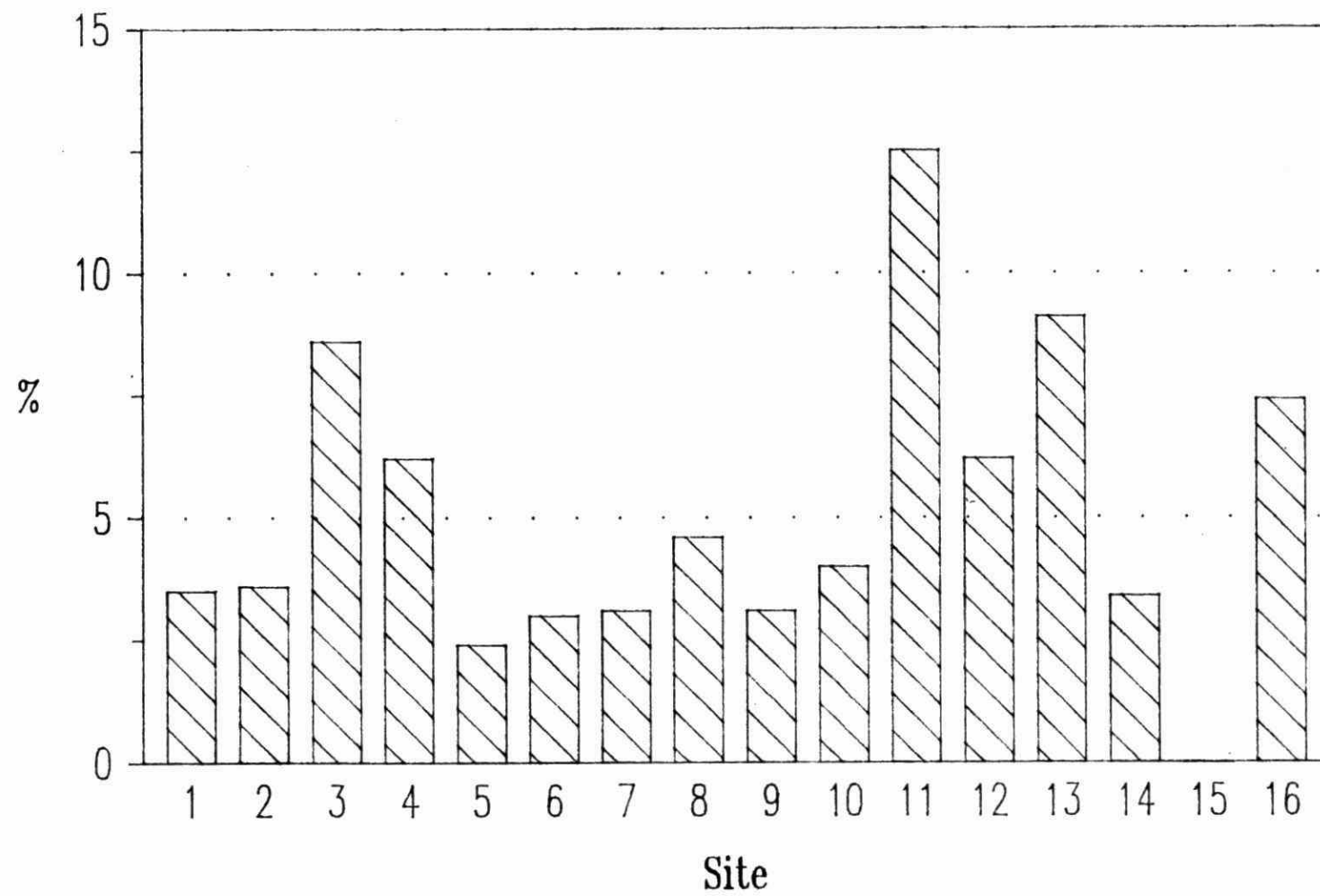


Fig. 7 Samples Not Submitted – Daily Precip. Network  
1980-81





**Fig. 8 Data Recovery – Aerochem Metrics Sampler  
1980-81**

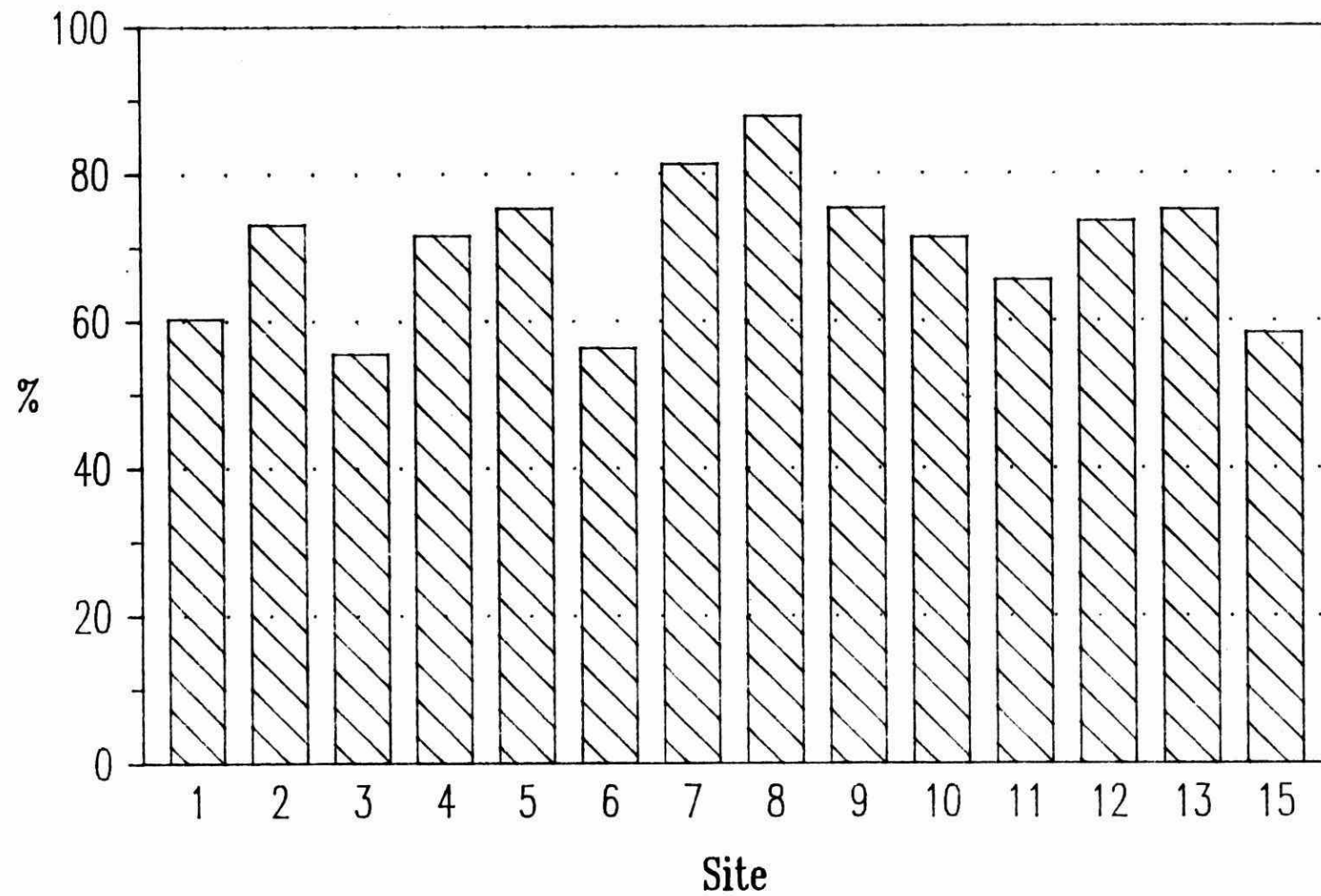


Fig. 9 Data Recovery – S.E.S. Sampler  
1980-81

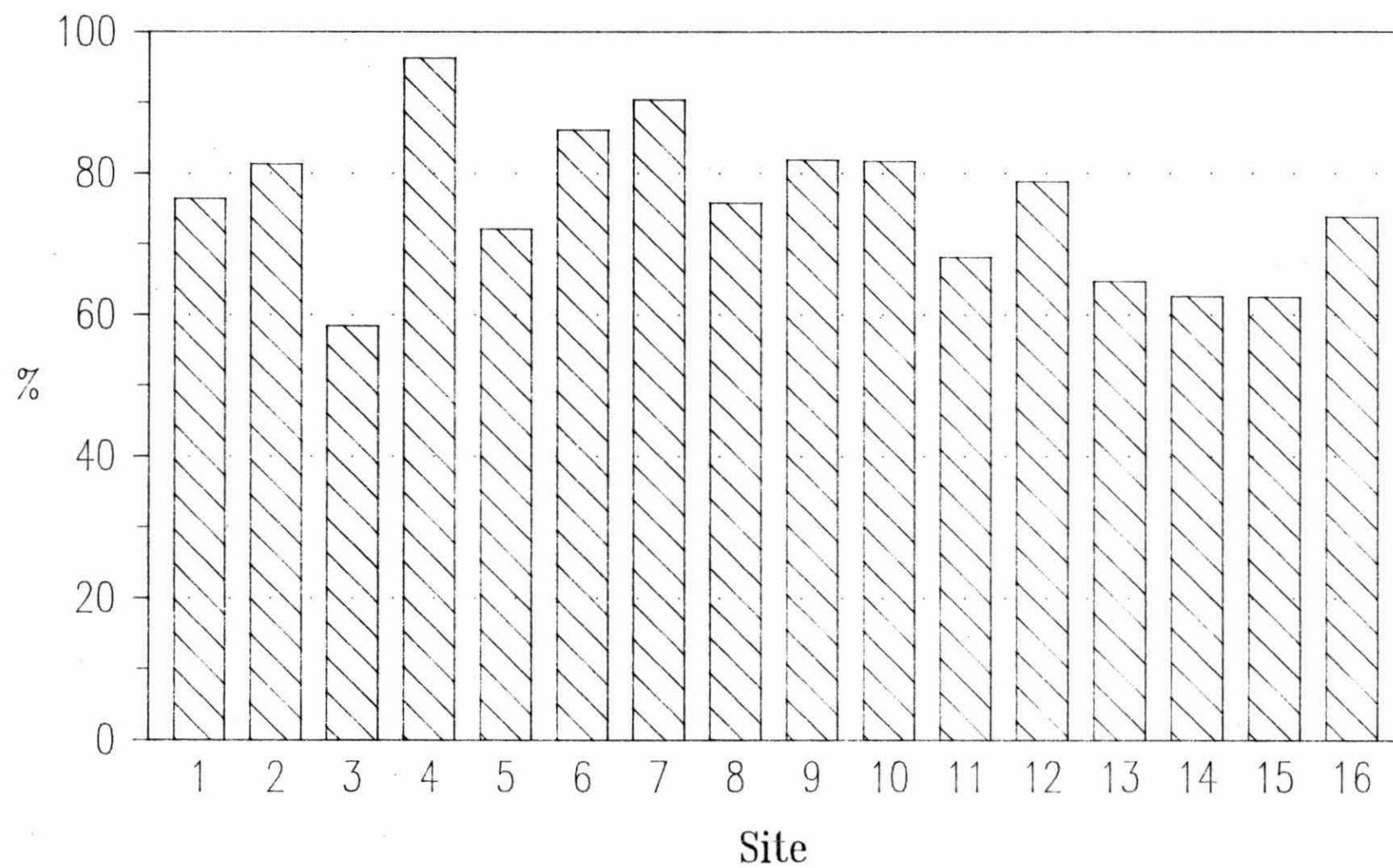


Fig. 10

A E R O C H E M   V S   S E S   P L O T S  
S T A T I O N = L O N G W O O D S

P L O T   O F   A \_ P H \* S \_ P H      L E G E N D :   A = 1   O B S . ,   B = 2   O B S . ,   E T C .

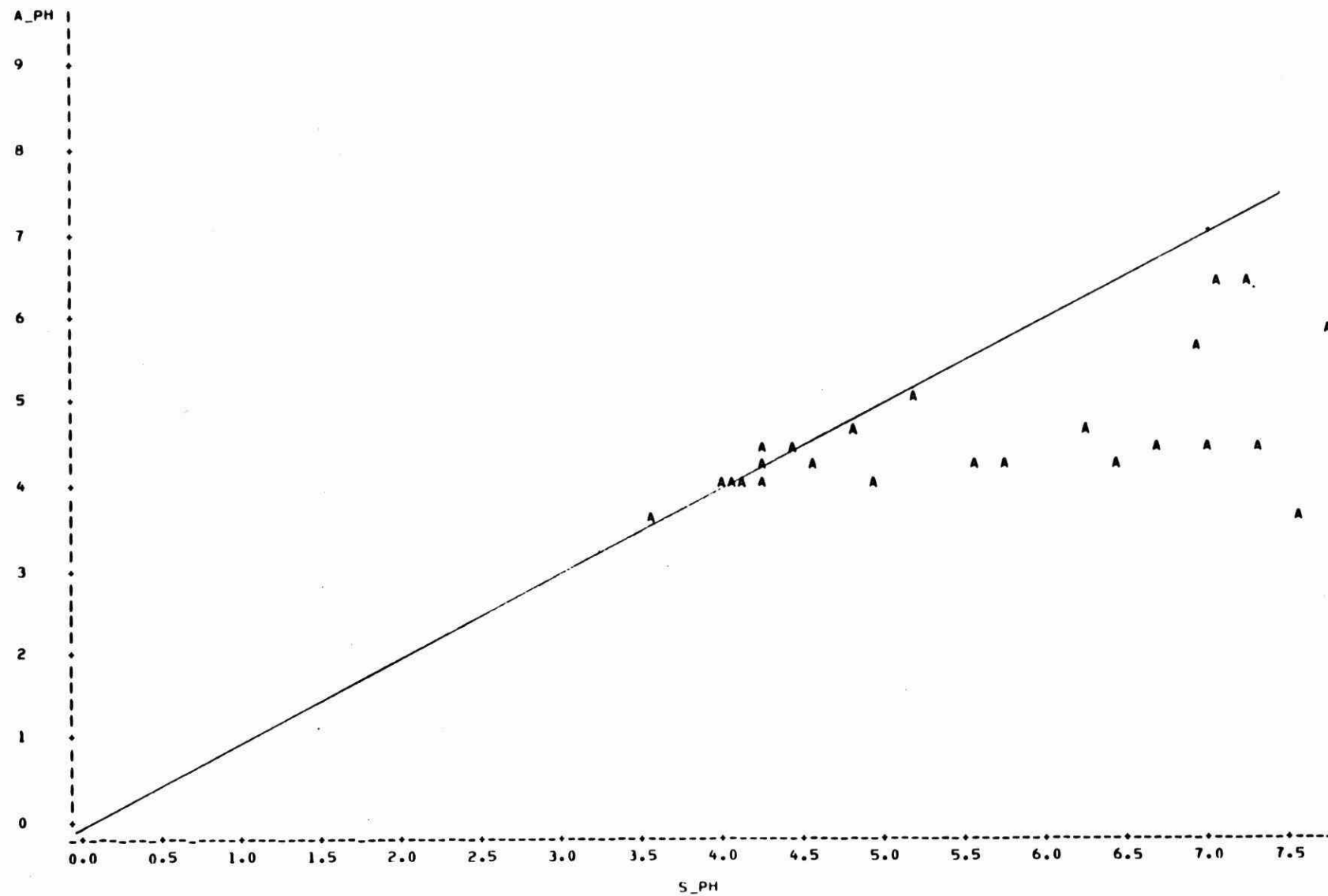


Fig. 11

A E R O C H E M   V S   S E S   P L O T S  
STATION=DORSET

PLOT OF A\_PH\*S\_PH      LEGEND: A = 1 OBS, B = 2 OBS, ETC.

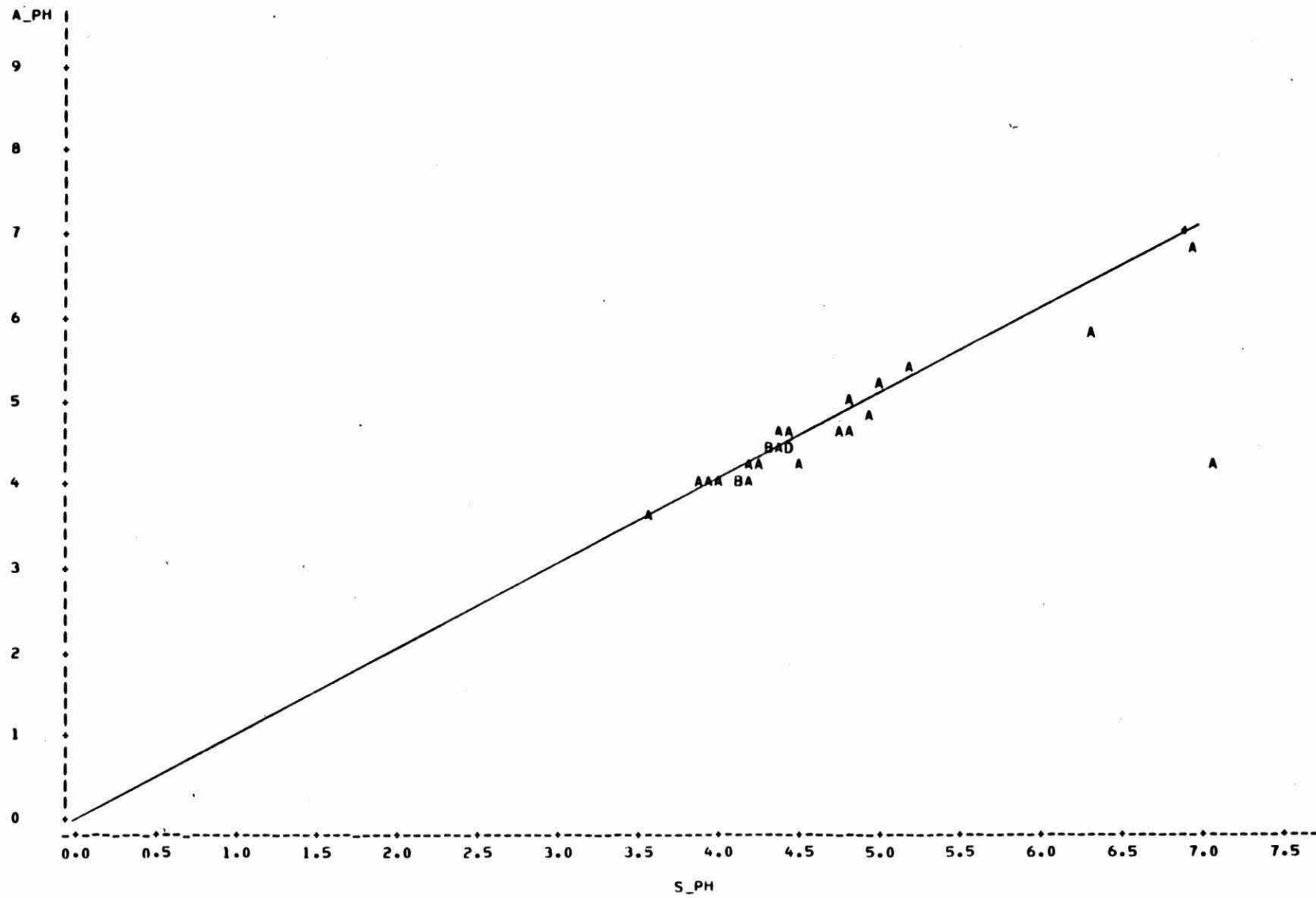


Fig. 12

A E R O C H E M   V S   S E S   P L O T S  
S T A T I O N = R A I L T O N

P L O T   O F   A \_ P H \* S \_ P H      L E G E N D :   A = 1   O B S ,   B = 2   O B S ,   E T C .

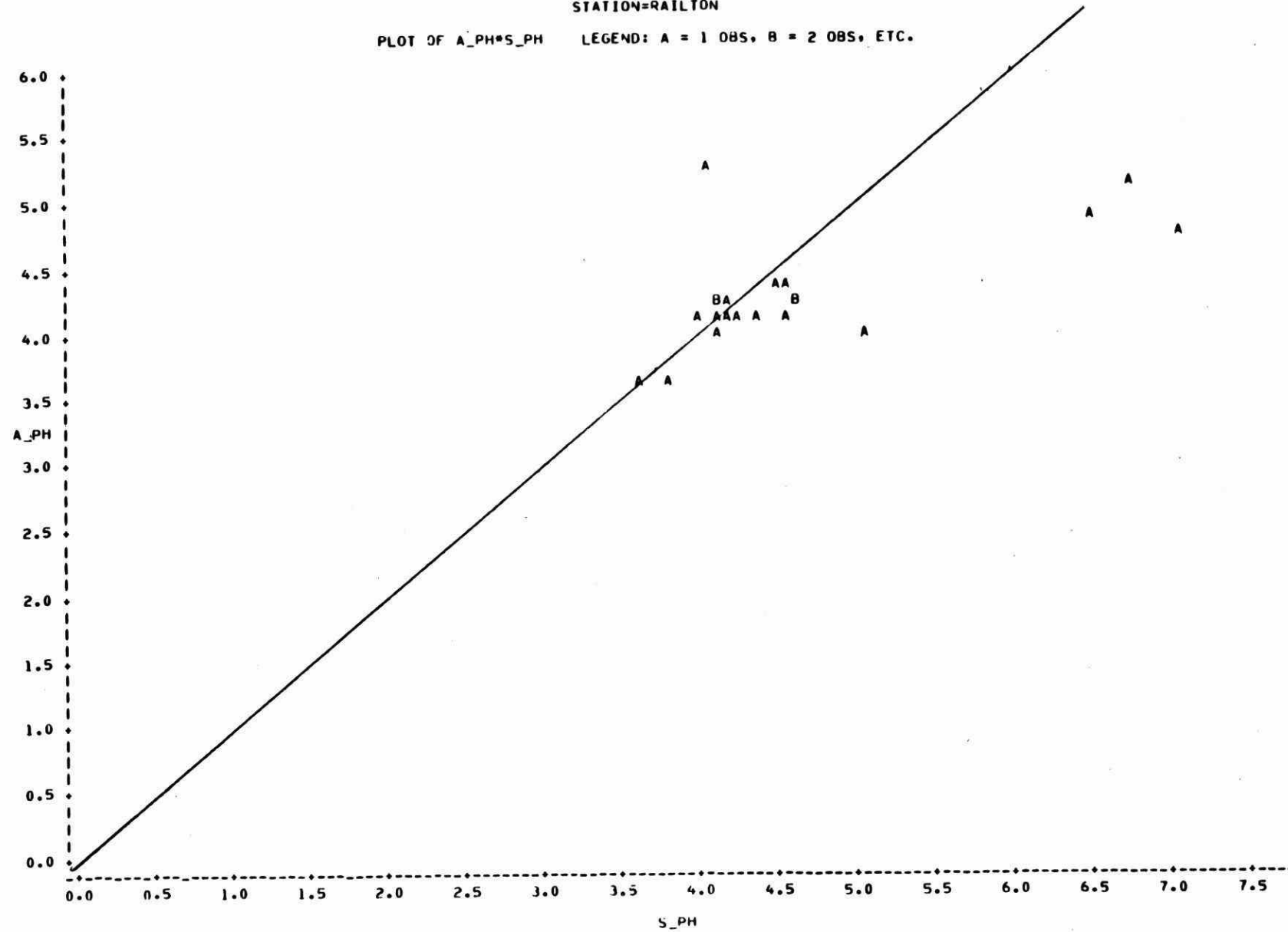
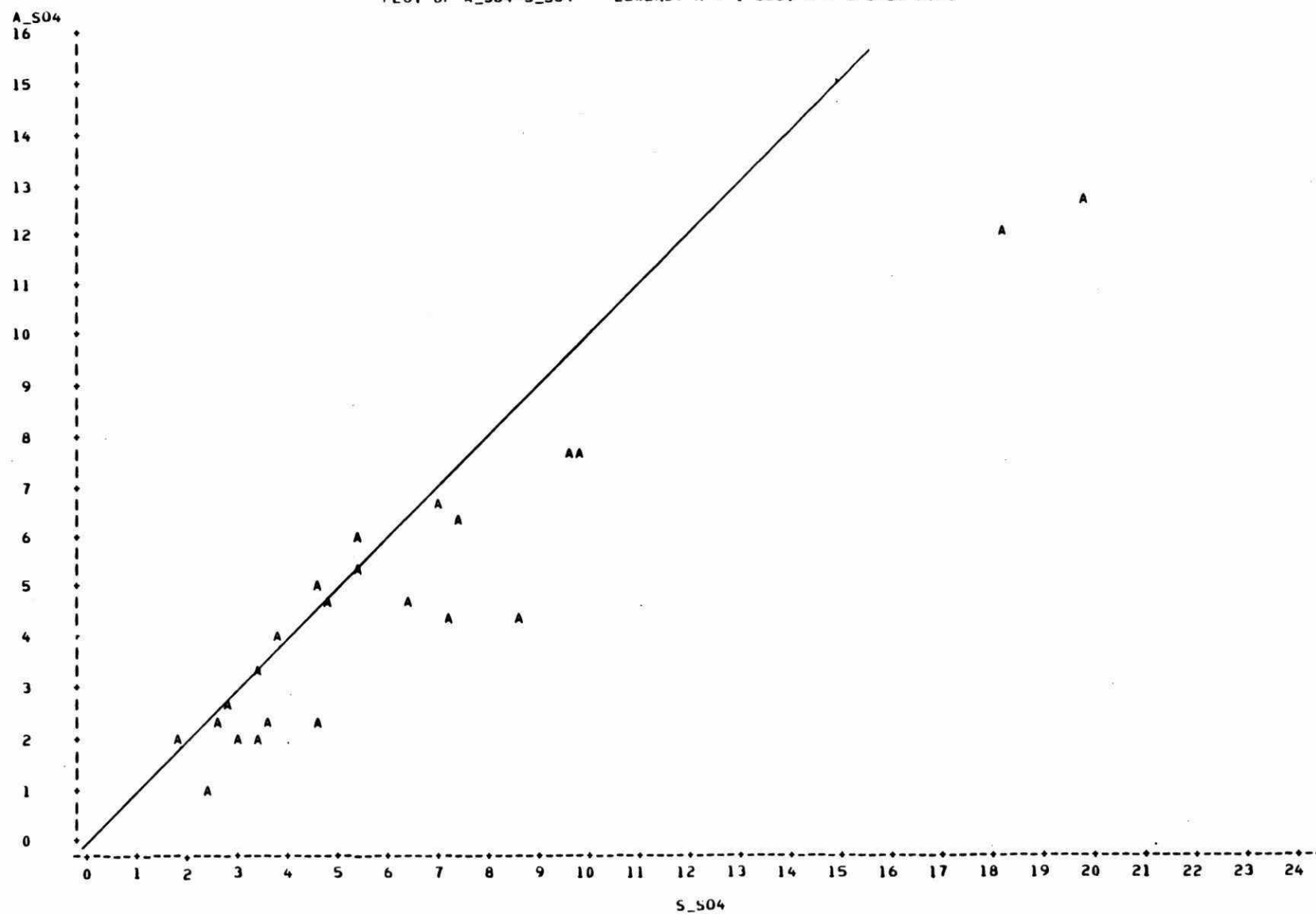


Fig. 13

A E R O C H E M   V S   S E S   P L O T S  
S T A T I O N = L O N G W O O D S

P L O T   O F   A \_ S O 4 \* S \_ S O 4      L E G E N D :   A = 1 O B S ,   B = 2 O B S ,   E T C .

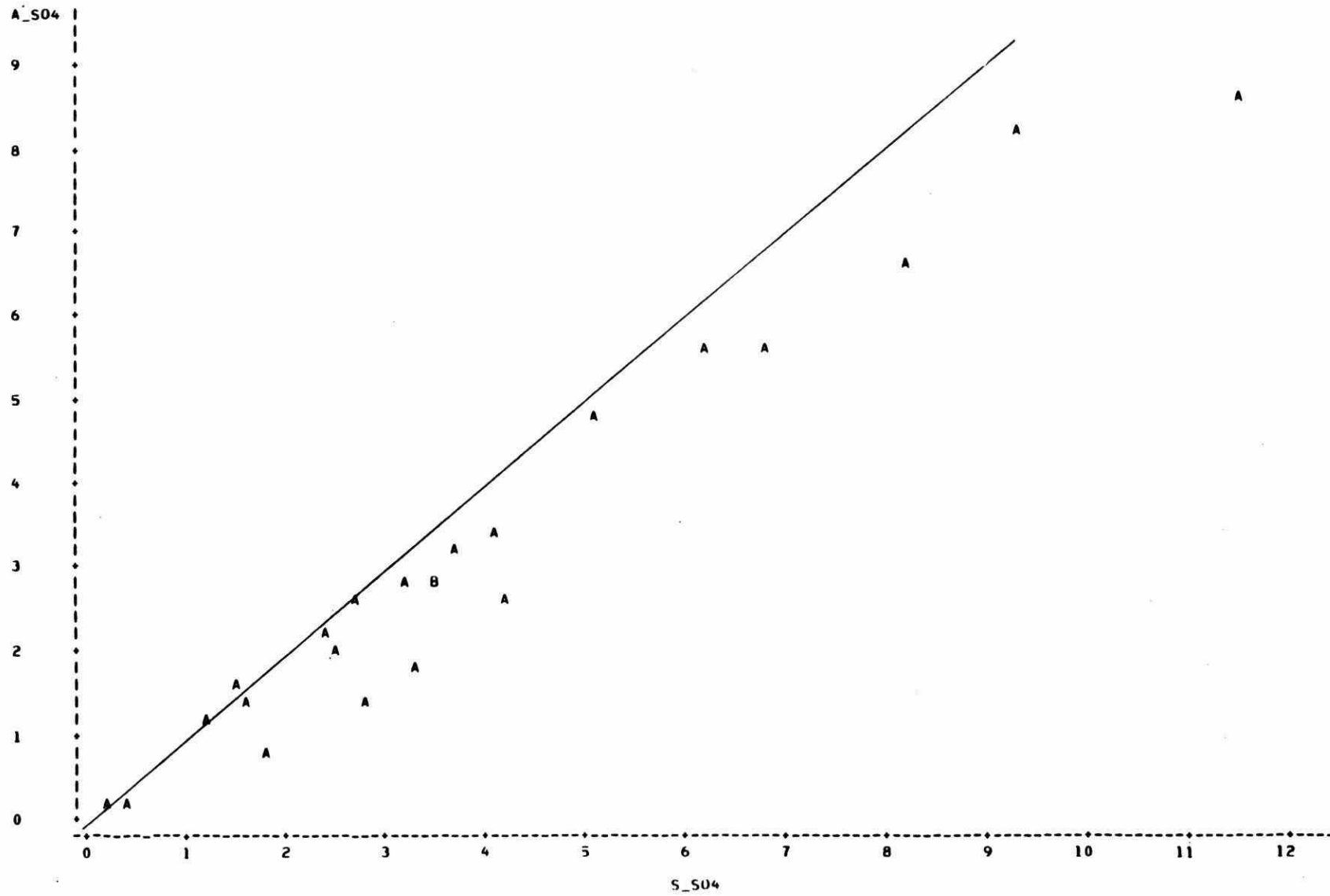


N O T E :      1 O B S H A D M I S S I N G V A L U E S

Fig. 14

A E R O C H E M   V S   S E S   P L O T S  
S T A T I O N = D O R S E T

P L O T   O F   A \_ S O 4 \* S \_ S O 4      L E G E N D :   A = 1 O B S ,   B = 2 O B S ,   E T C .

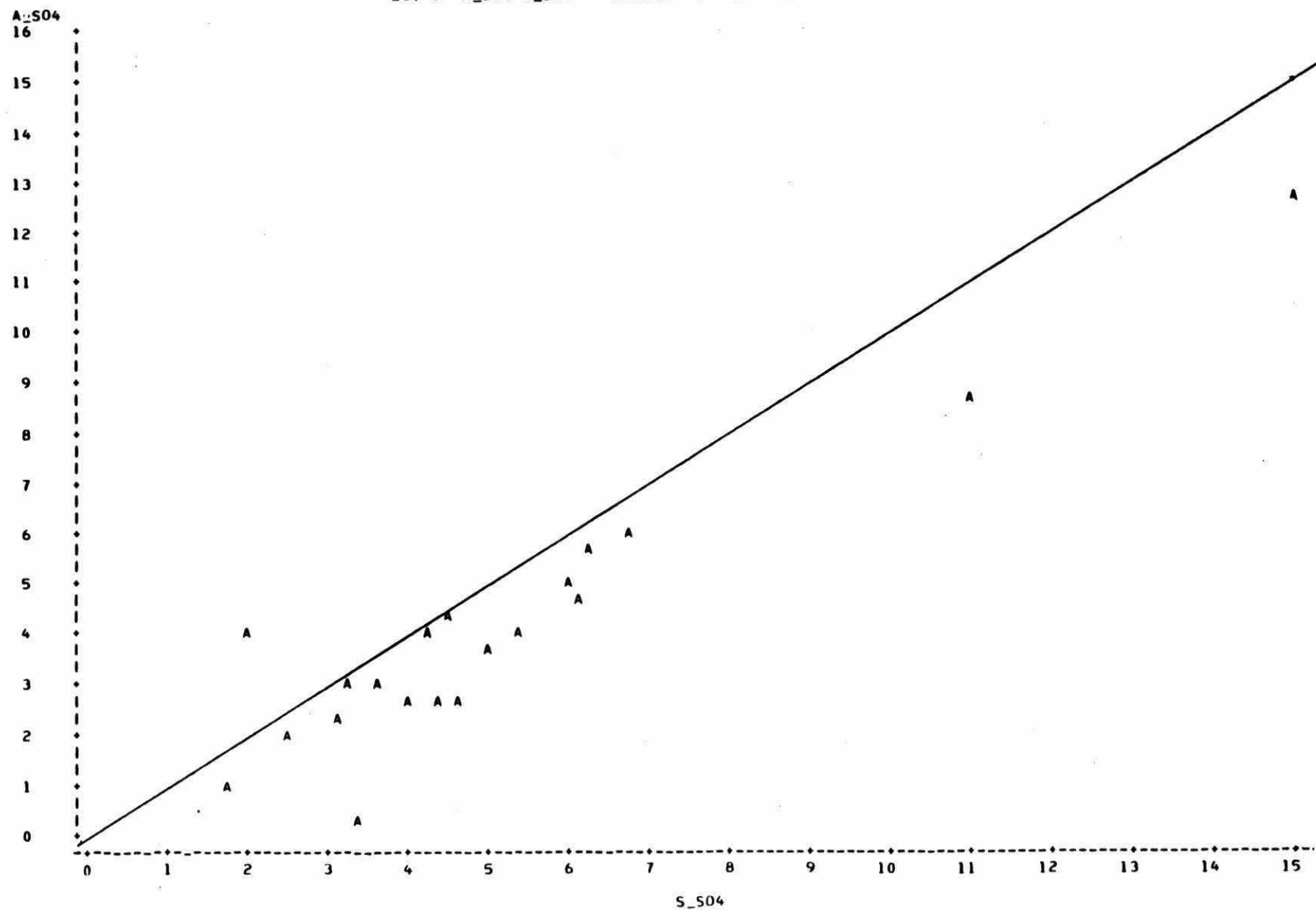


N O T E :      5 O B S H A D M I S S I N G V A L U E S

Fig. 15

A E R O C H E M   V S   S E S   P L O T S  
S T A T I O N = R A I L T O N

P L O T   O F   A \_ S O 4 \* S \_ S O 4      L E G E N D :   A = 1 O B S ,   B = 2 O B S ,   E T C .



N O T E :      1 O B S H A D M I S S I N G V A L U E S

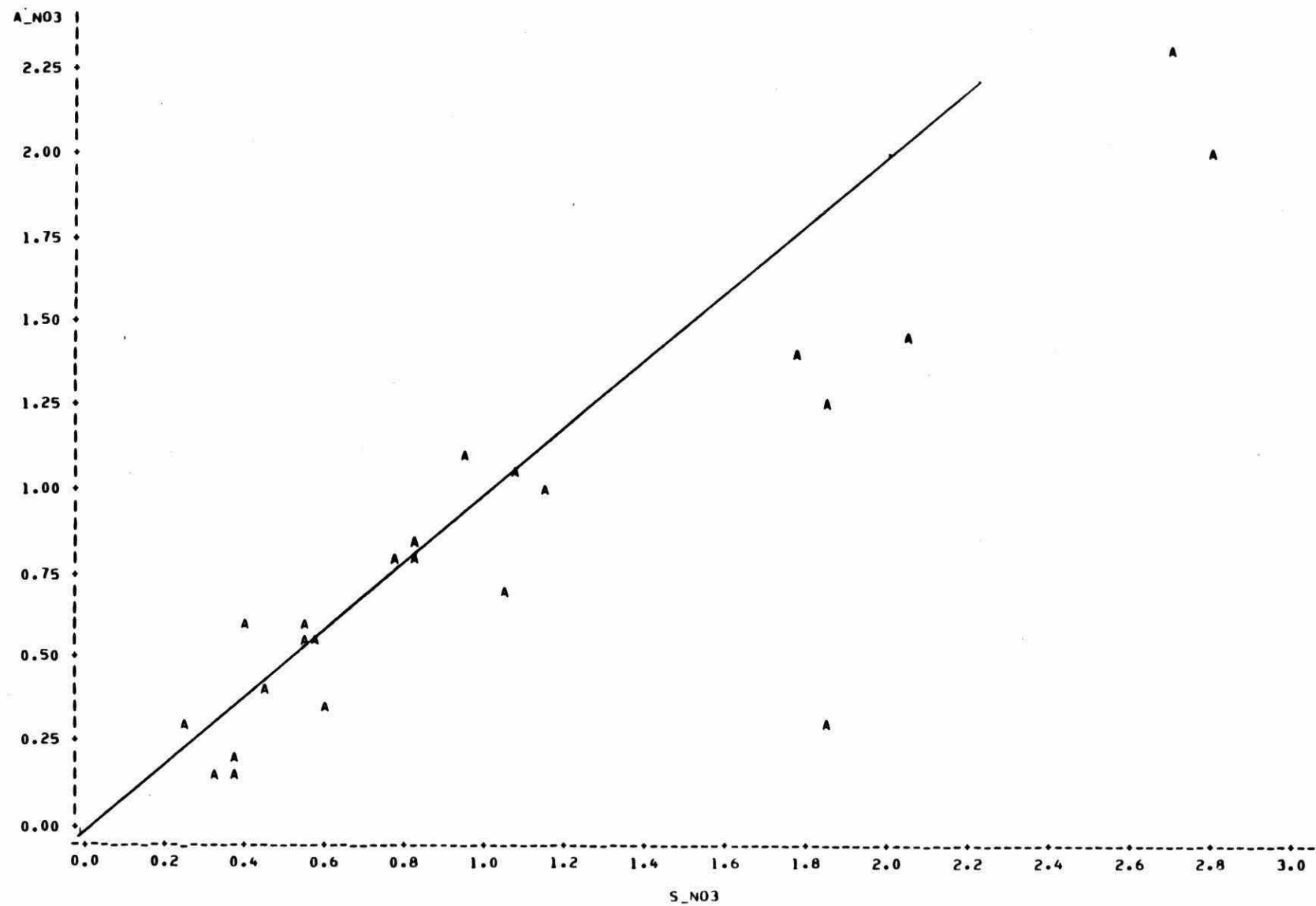


Fig. 16

A E R O C H E M V S S E S P L O T S

STATION=LONGWOODS

PLOT OF A\_N03\*S\_N03 LEGEND: A = 1 OBS, B = 2 OBS, ETC.



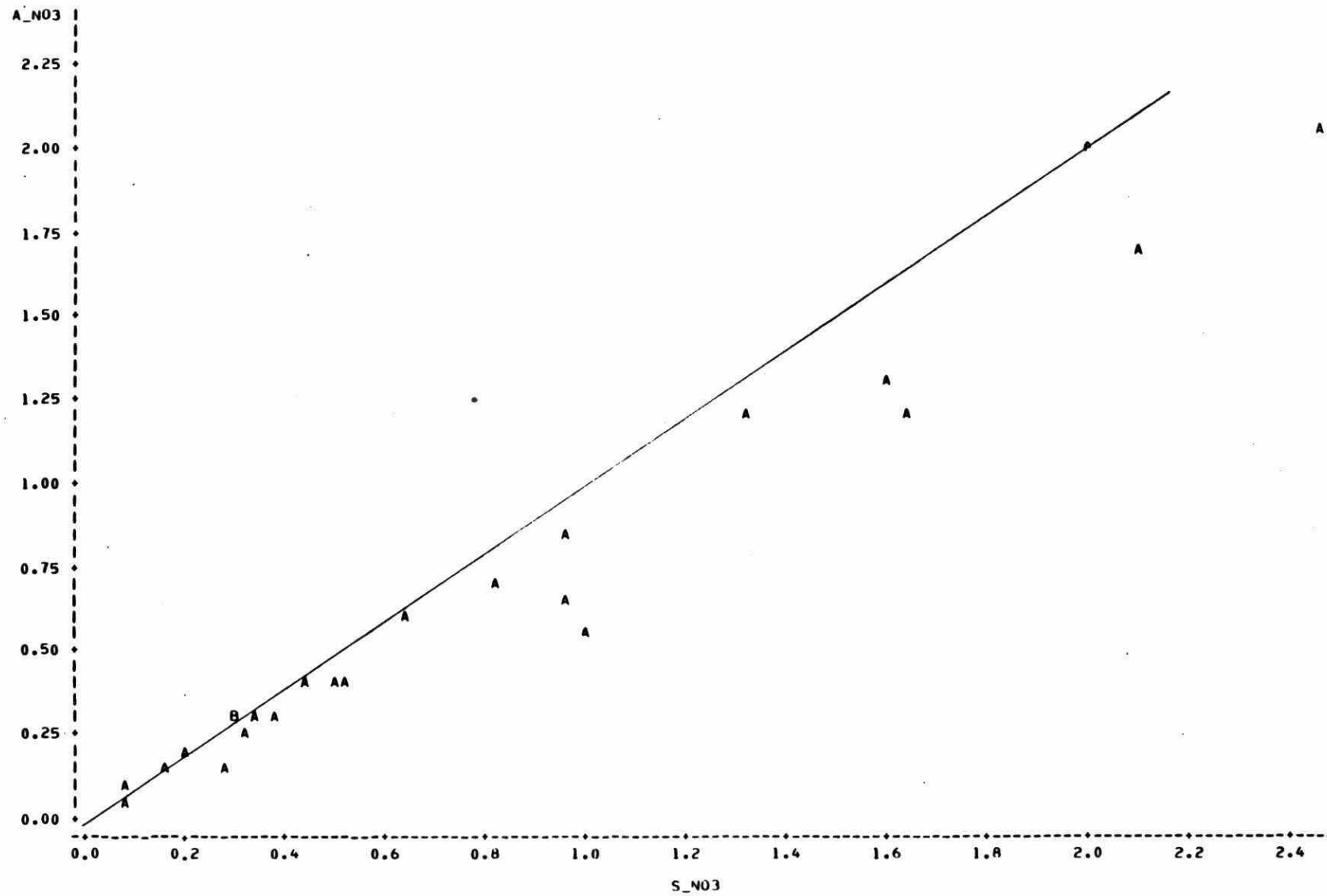
NOTE: 1 OBS HAD MISSING VALUES

Fig. 17

A E R O C H E M   V S   S E S   P L O T S

STATION=DORSET

PLOT OF A\_N03\*S\_N03      LEGEND: A = 1 OBS, B = 2 OBS, ETC.

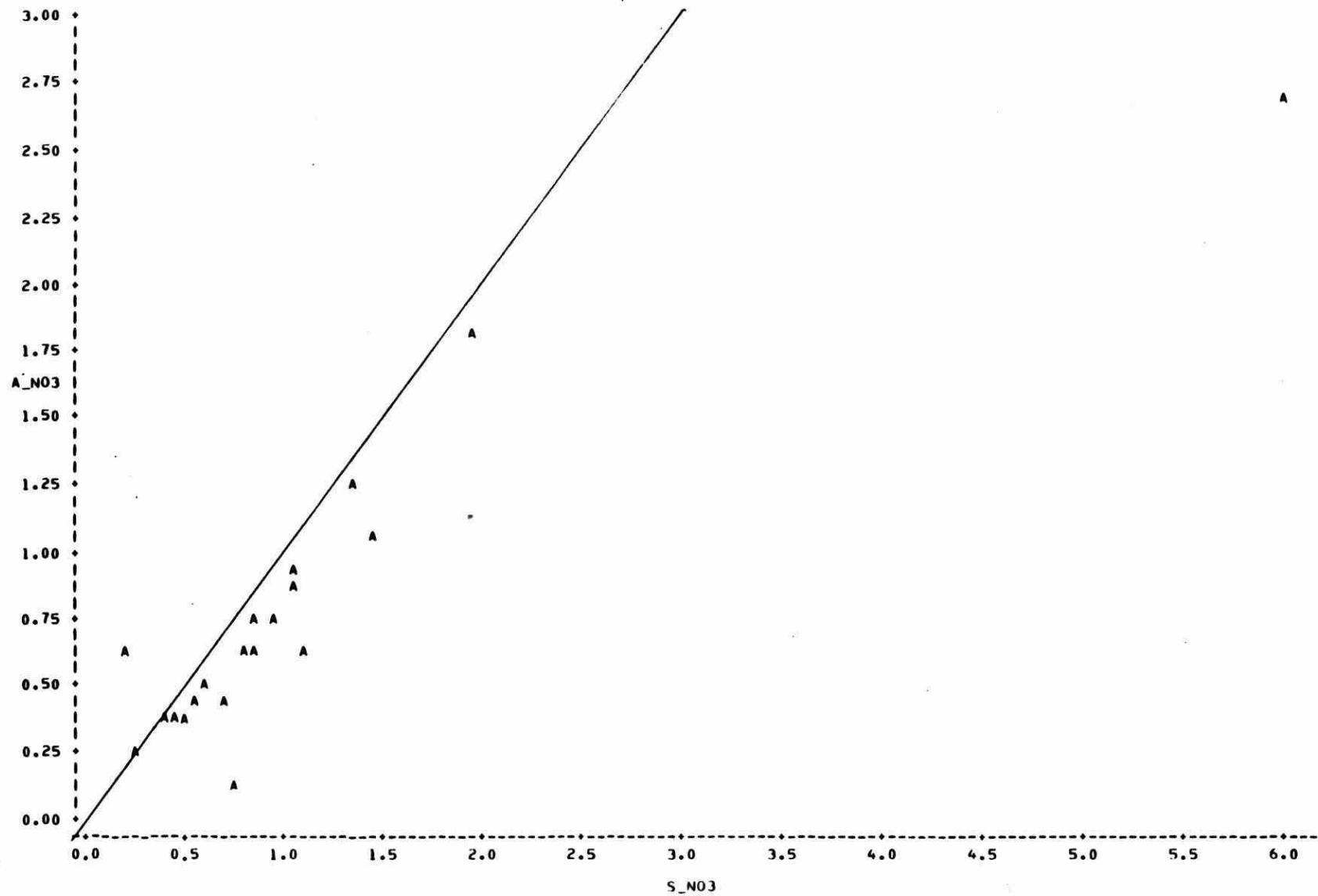


NOTE: 5 OBS HAD MISSING VALUES

Fig. 18

AEROCHEM VS SES PLOTS  
STATION=RAILTON

PLOT OF A\_N03\*S\_N03 LEGEND: A = 1 OBS, B = 2 OBS, ETC.

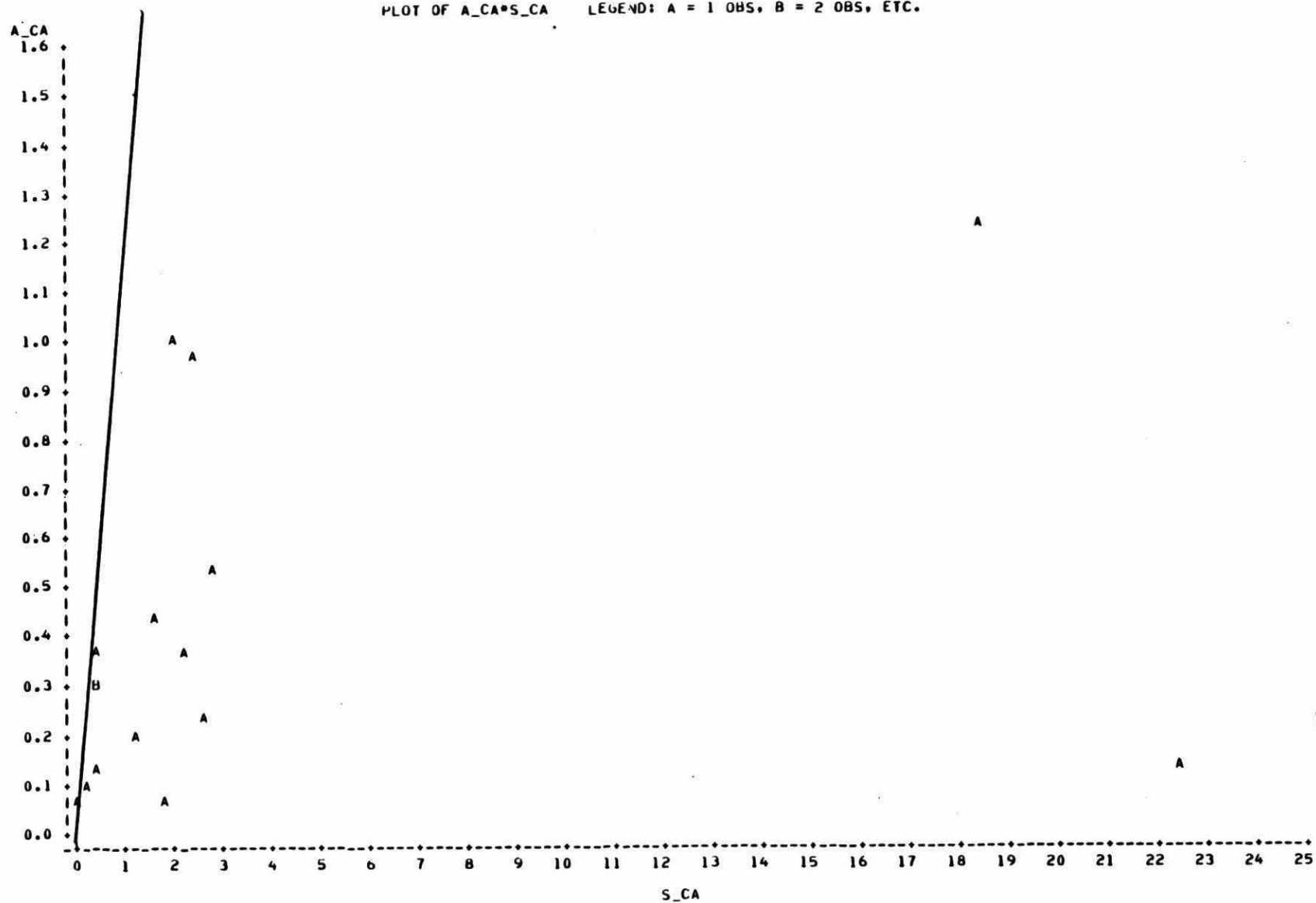


NOTE: 1 OBS HAD MISSING VALUES

Fig. 19

AEROCHEM VS SES PLOTS  
STATION=LONGWOODS

PLOT OF A\_CA\*S\_CA    LEGEND: A = 1 OBS, B = 2 OBS, ETC.

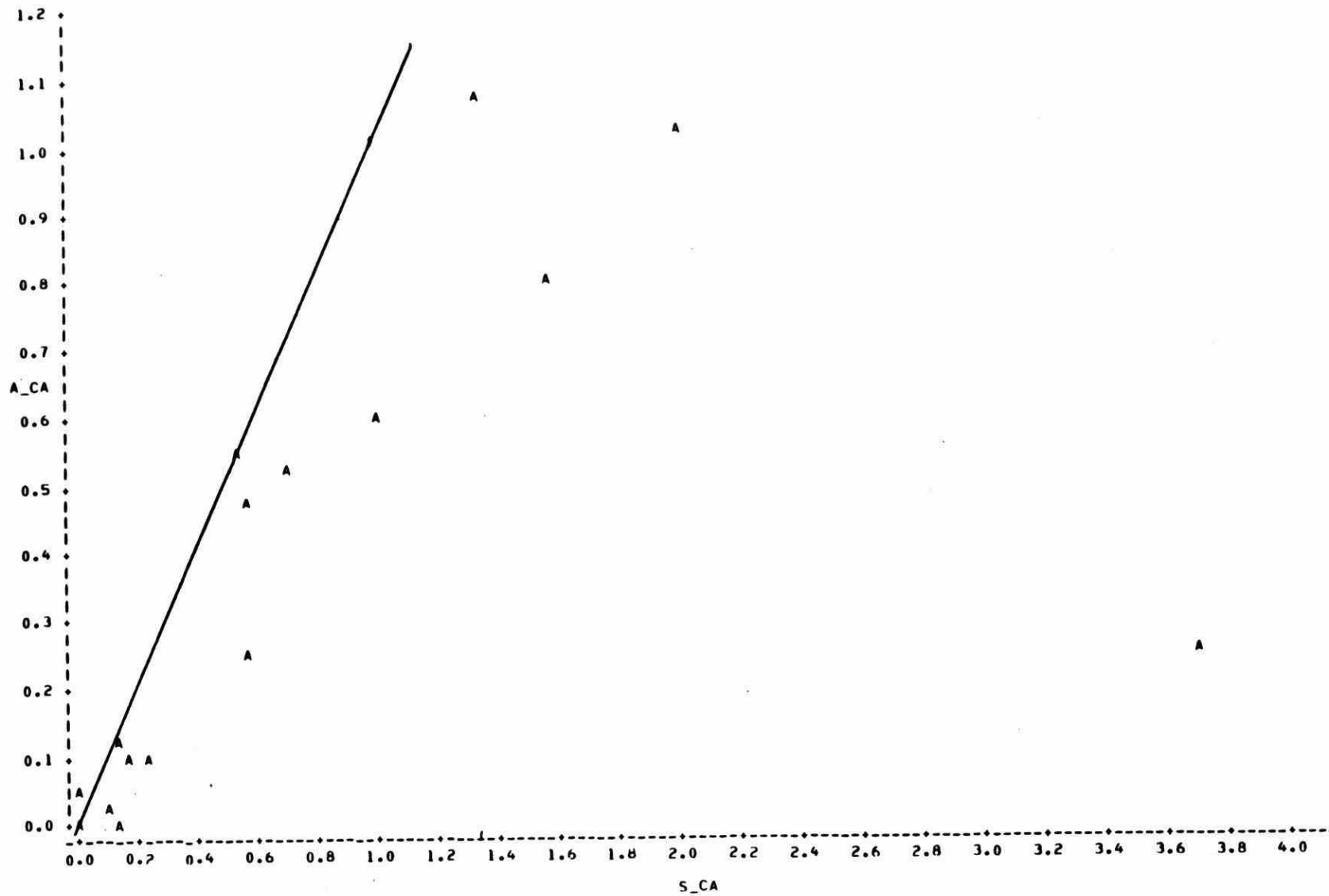


NOTE: 8 OBS HAD MISSING VALUES

Fig. 20

A E R O C H E M   V S   S E S   P L O T S  
STATION=DORSET

PLOT OF A\_CA\*S\_CA      LEGEND: A = 1 OBS, B = 2 OBS, ETC.

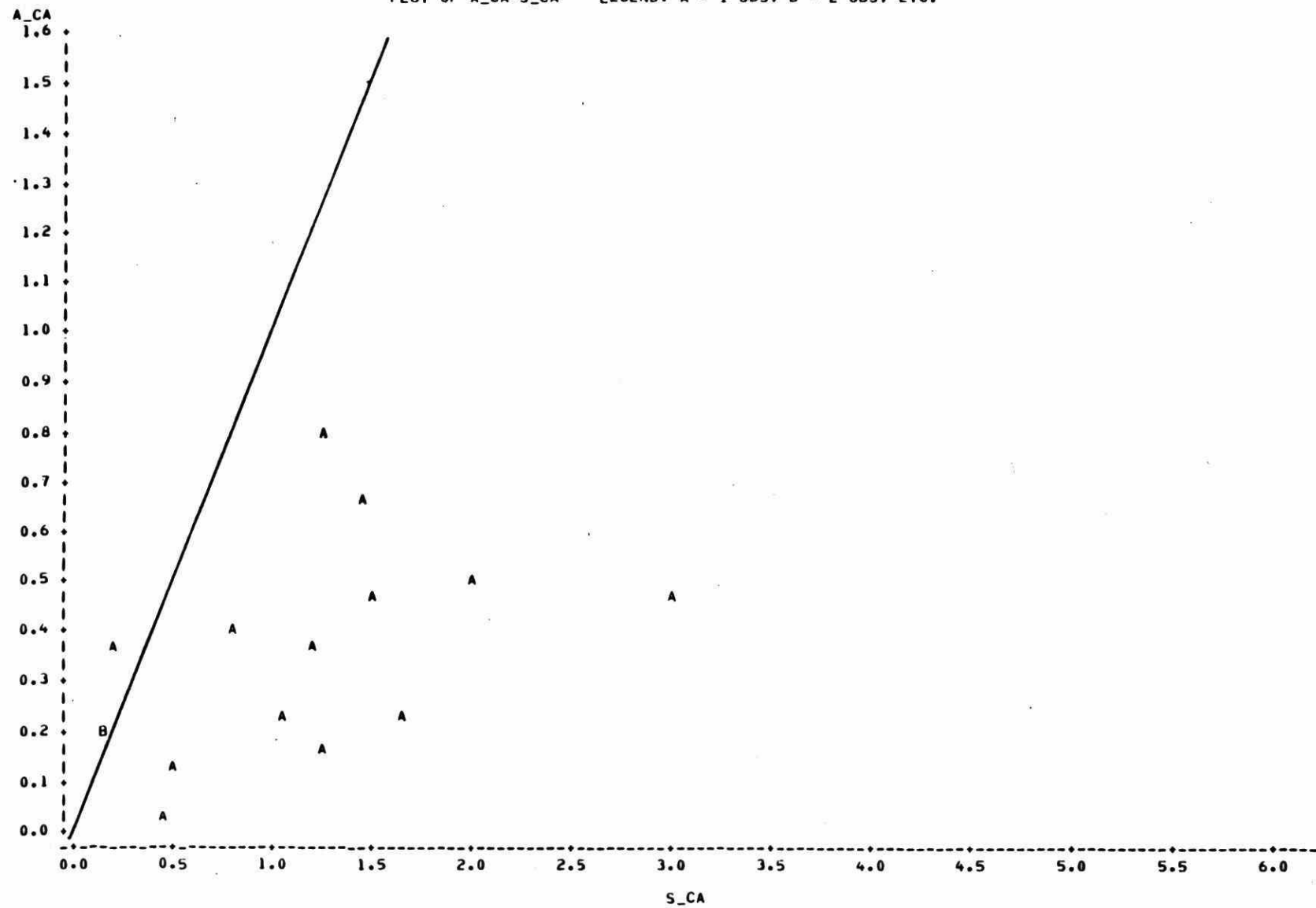


NOTE: 12 OBS HAD MISSING VALUES

Fig. 21

A E R O C H E M   V S   S E S   P L O T S  
S T A T I O N = R A I L T O N

P L O T   O F   A \_ C A \* S \_ C A      L E G E N D :   A = 1 O B S ,   B = 2 O B S ,   E T C .

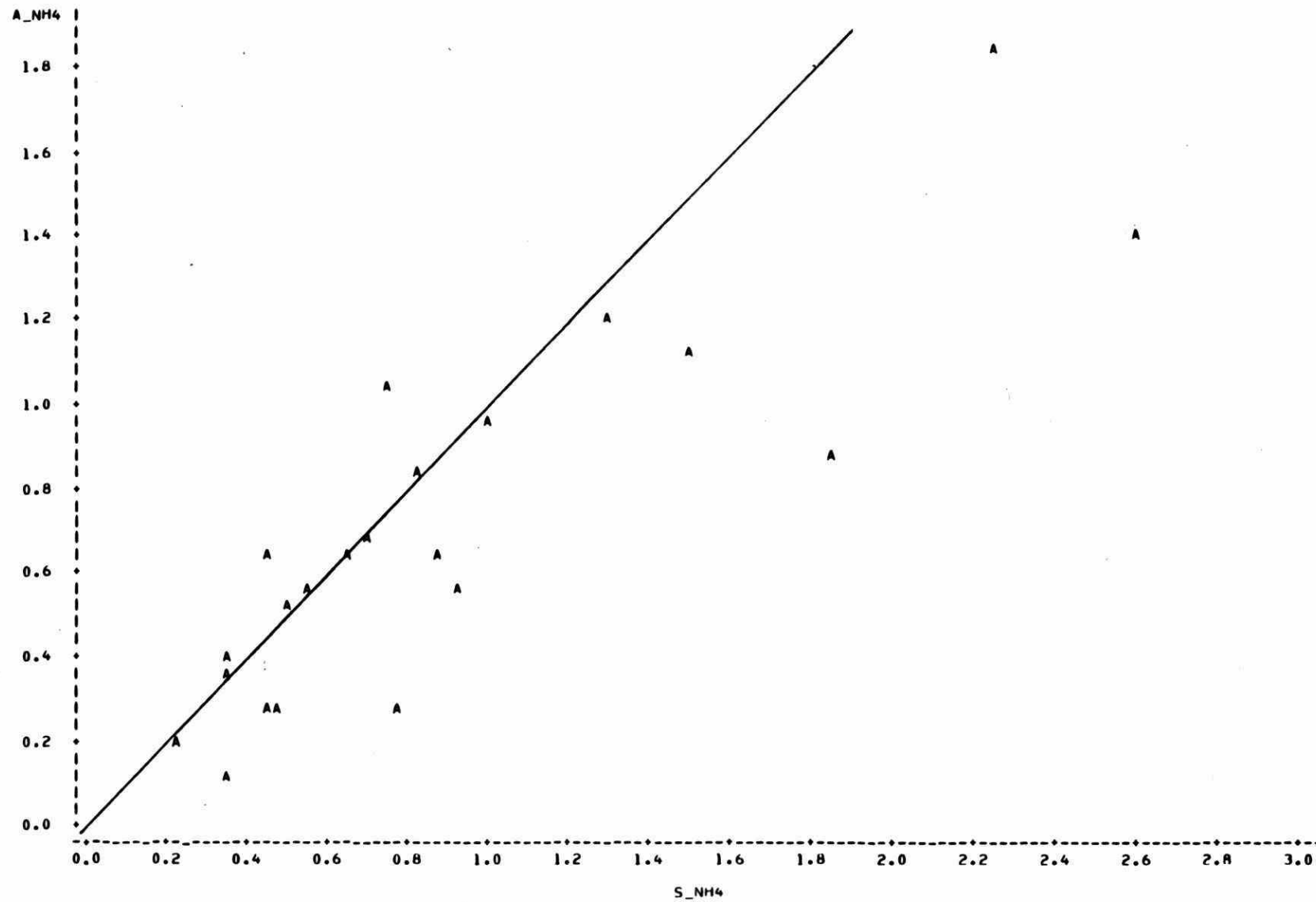


N O T E :      6 O B S H A D M I S S I N G V A L U E S

Fig. 22

A E R O C H E M   V S   S E S   P L O T S  
STATION=LONGWOODS

PLOT OF A\_NH4\*S\_NH4    LEGEND: A = 1 OBS, B = 2 OBS, ETC.

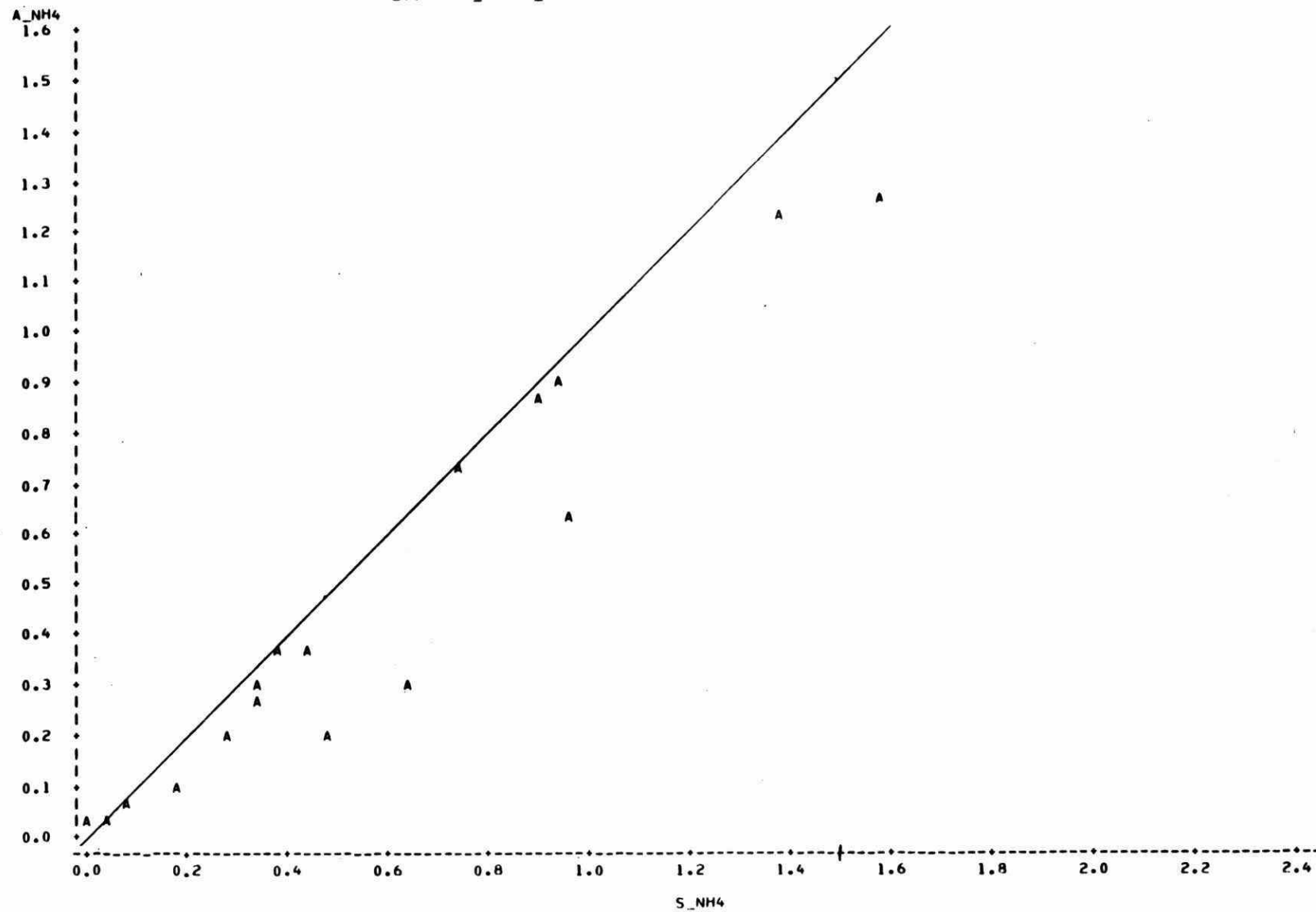


NOTE: 2 OBS HAD MISSING VALUES

Fig. 23

A E R O C H E M   V S   S E S   P L O T S  
S T A T I O N = D O R S E T

P L O T   O F   A \_ N H 4 \* S \_ N H 4      L E G E N D :   A = 1 O B S ,   B = 2 O B S ,   E T C .



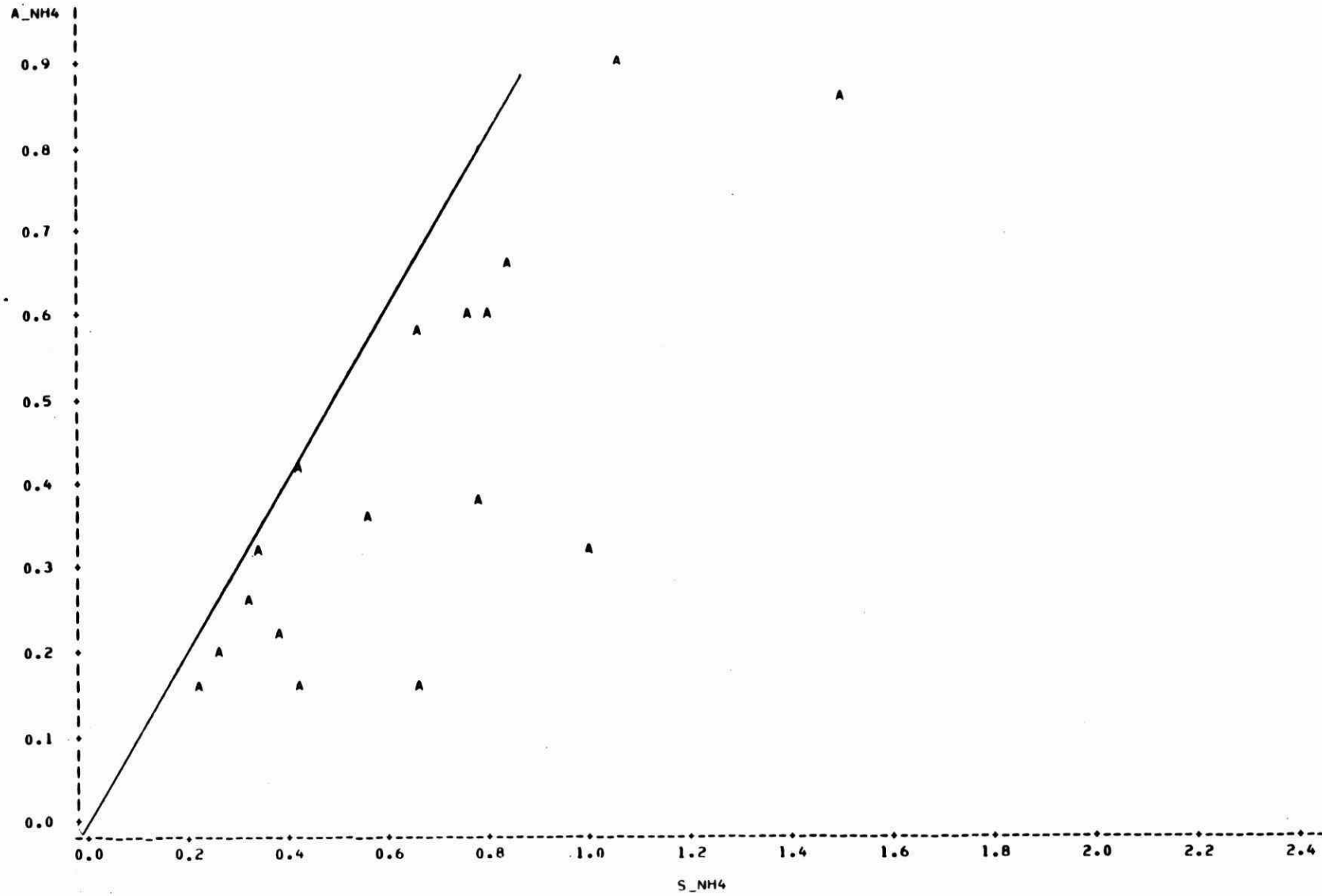
N O T E :      11 O B S H A D M I S S I N G V A L U E S



Fig. 24

AEROCHEM VS SES PLOTS  
STATION=RAILTON

PLOT OF A\_NH4\*S\_NH4      LEGEND: A = 1 OBS, B = 2 OBS, ETC.



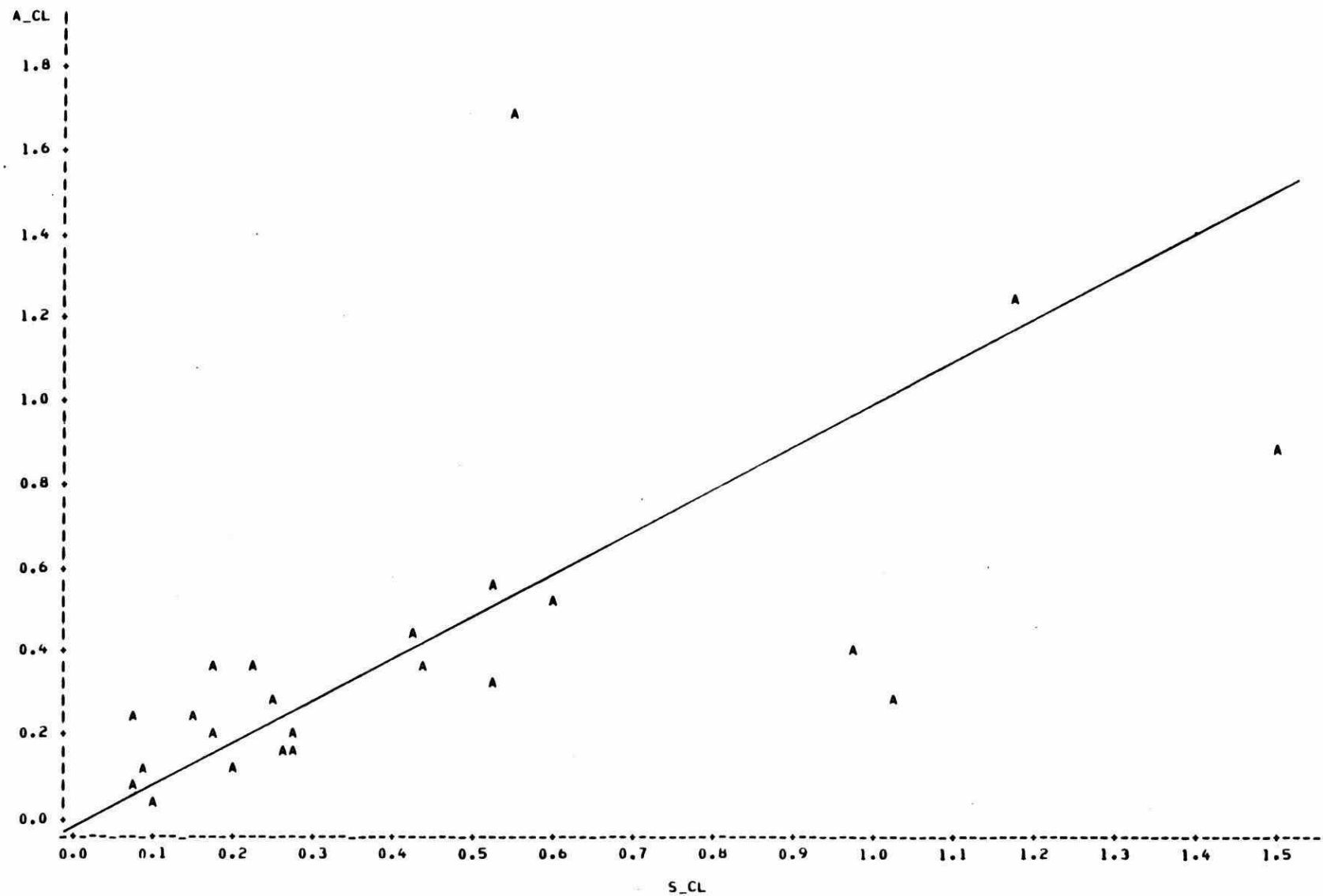
NOTE: 4 OBS HAD MISSING VALUES

Fig. 25

AEROCHEM VS SES PLOTS

STATION=LONGWOODS

PLOT OF A\_CL\*S\_CL      LEGEND: A = 1 OBS, B = 2 OBS, ETC.

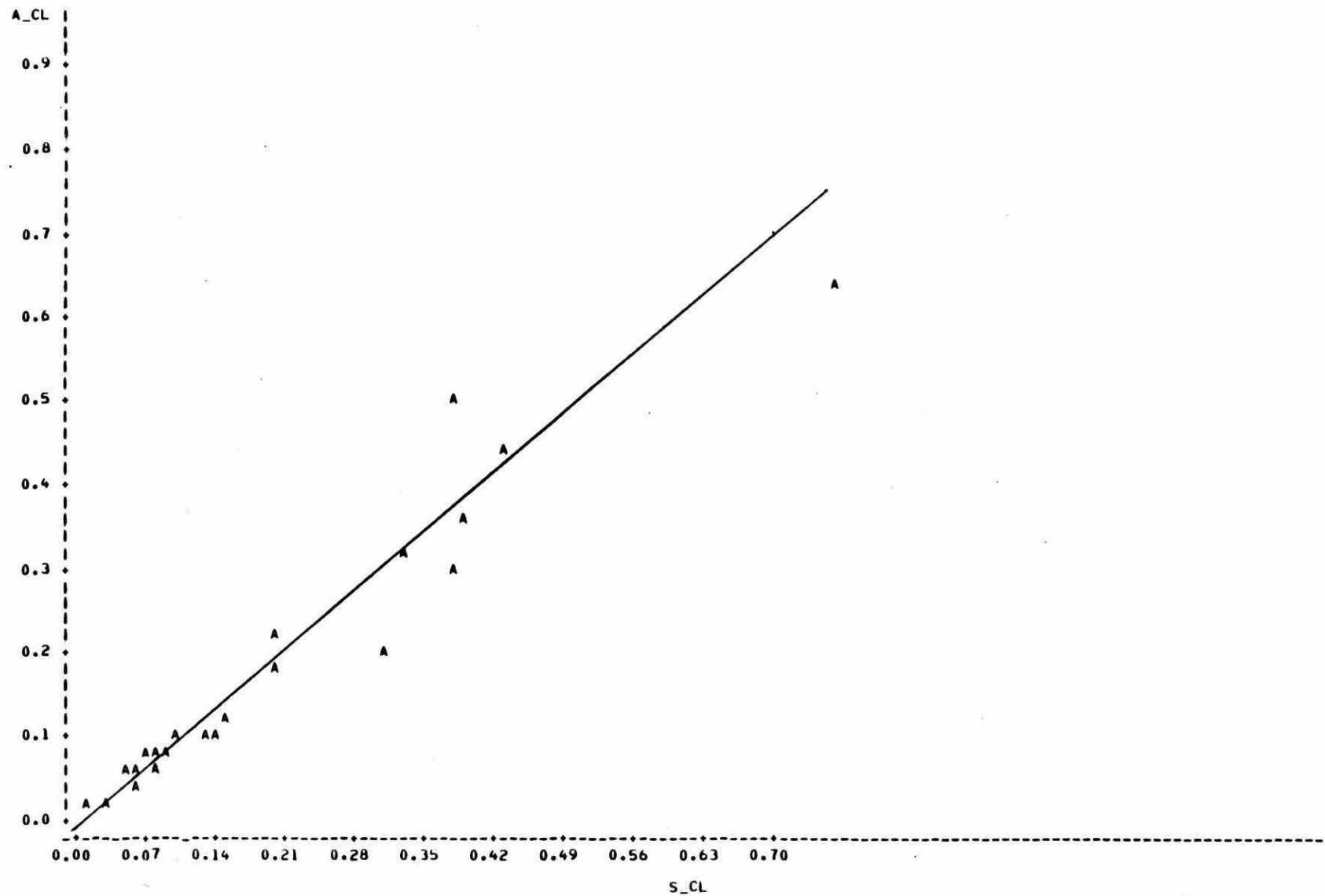


NOTE: 1 OBS HAD MISSING VALUES

Fig. 26

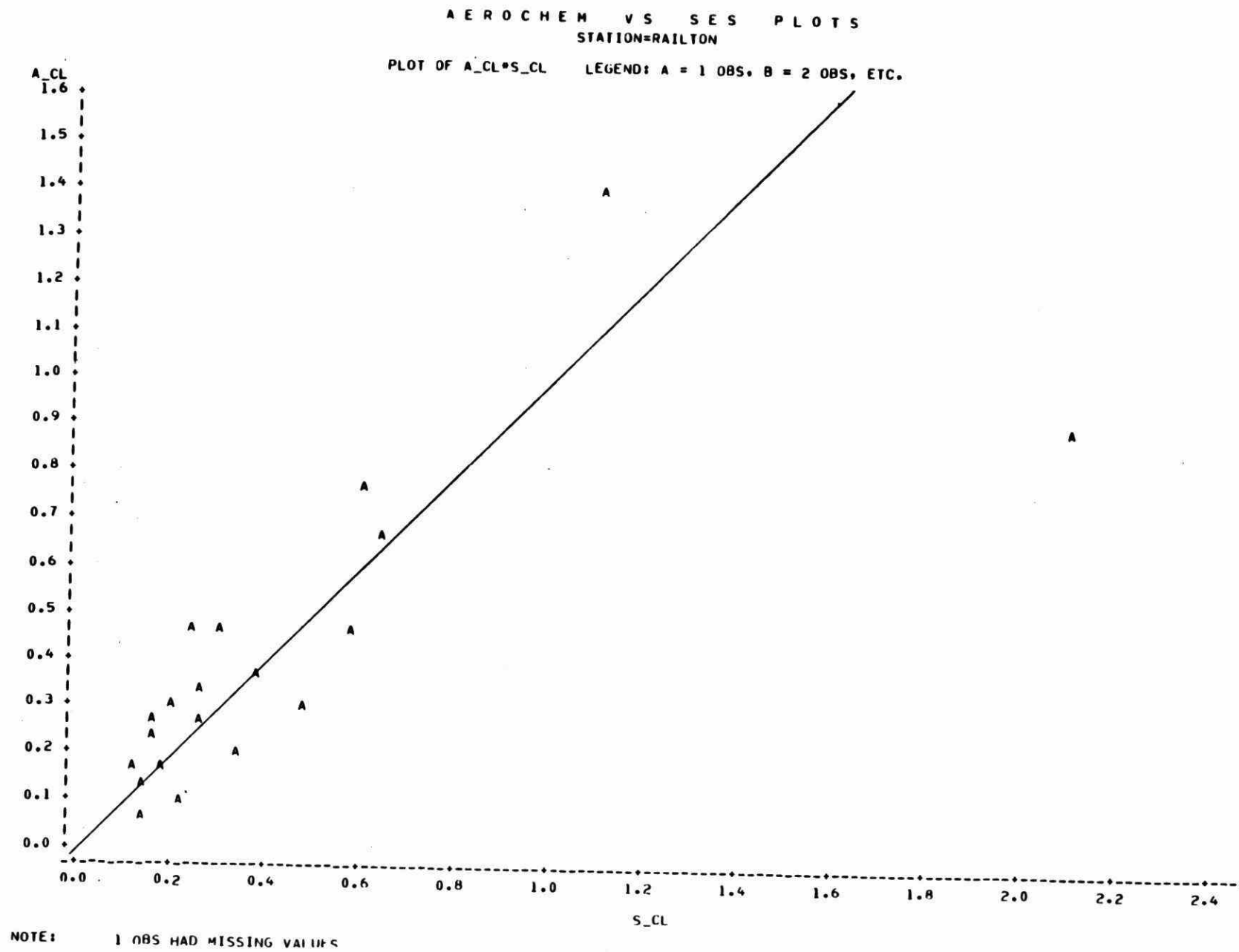
A E R O C H E M   V S   S E S   P L O T S  
S T A T I O N = D O R S E T

P L O T   O F   A \_ C L \* S \_ C L      L E G E N D :   A = 1 O B S ,   B = 2 O B S ,   E T C .

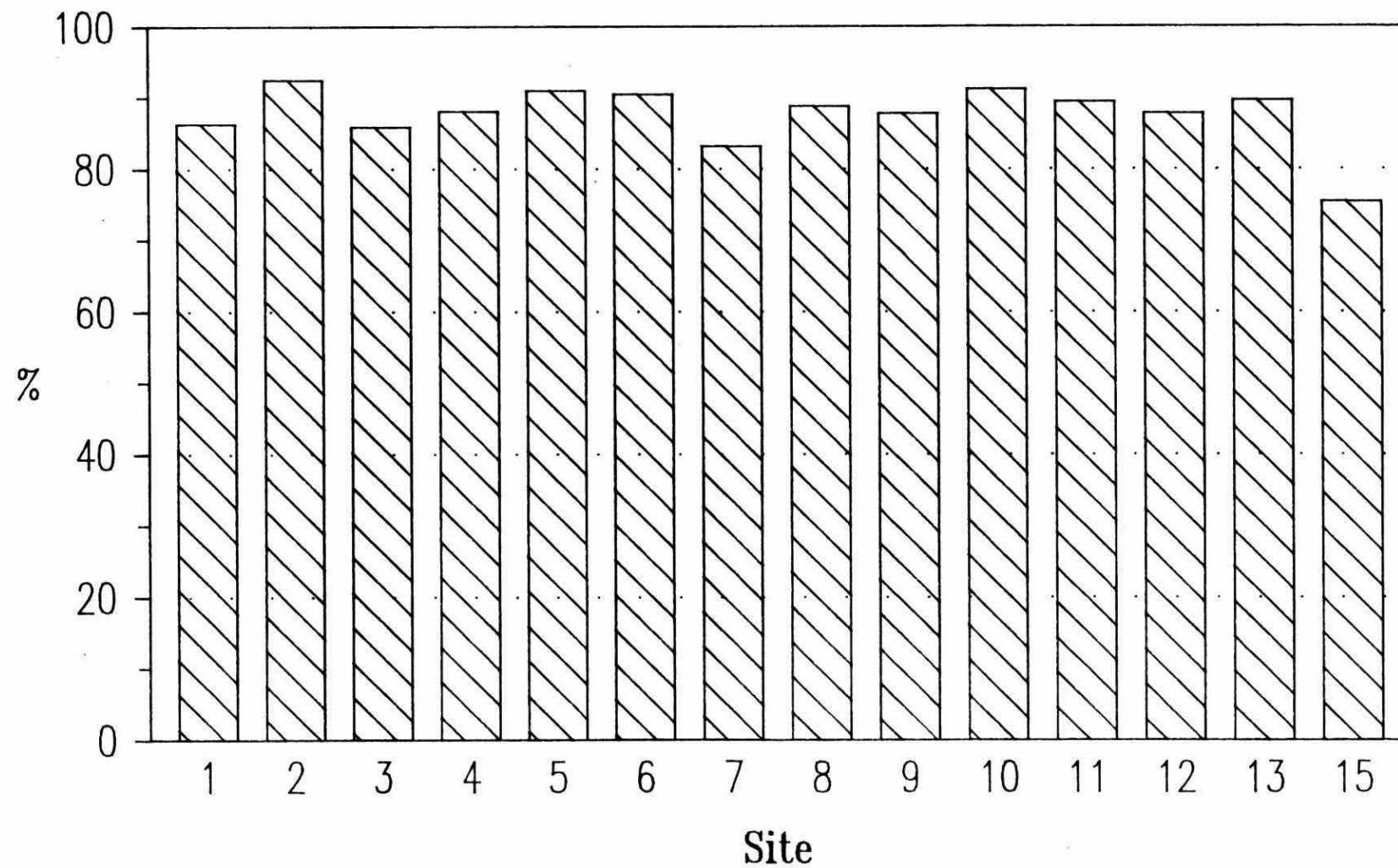


N O T E :      6 O B S H A D M I S S I N G V A L U E S

Fig. 27



**Fig. 28 Sampling Efficiency – Aerochem Metrics Sampler  
1981**



**Fig. 29 Sampling Efficiency – S.E.S. Sampler  
1981**

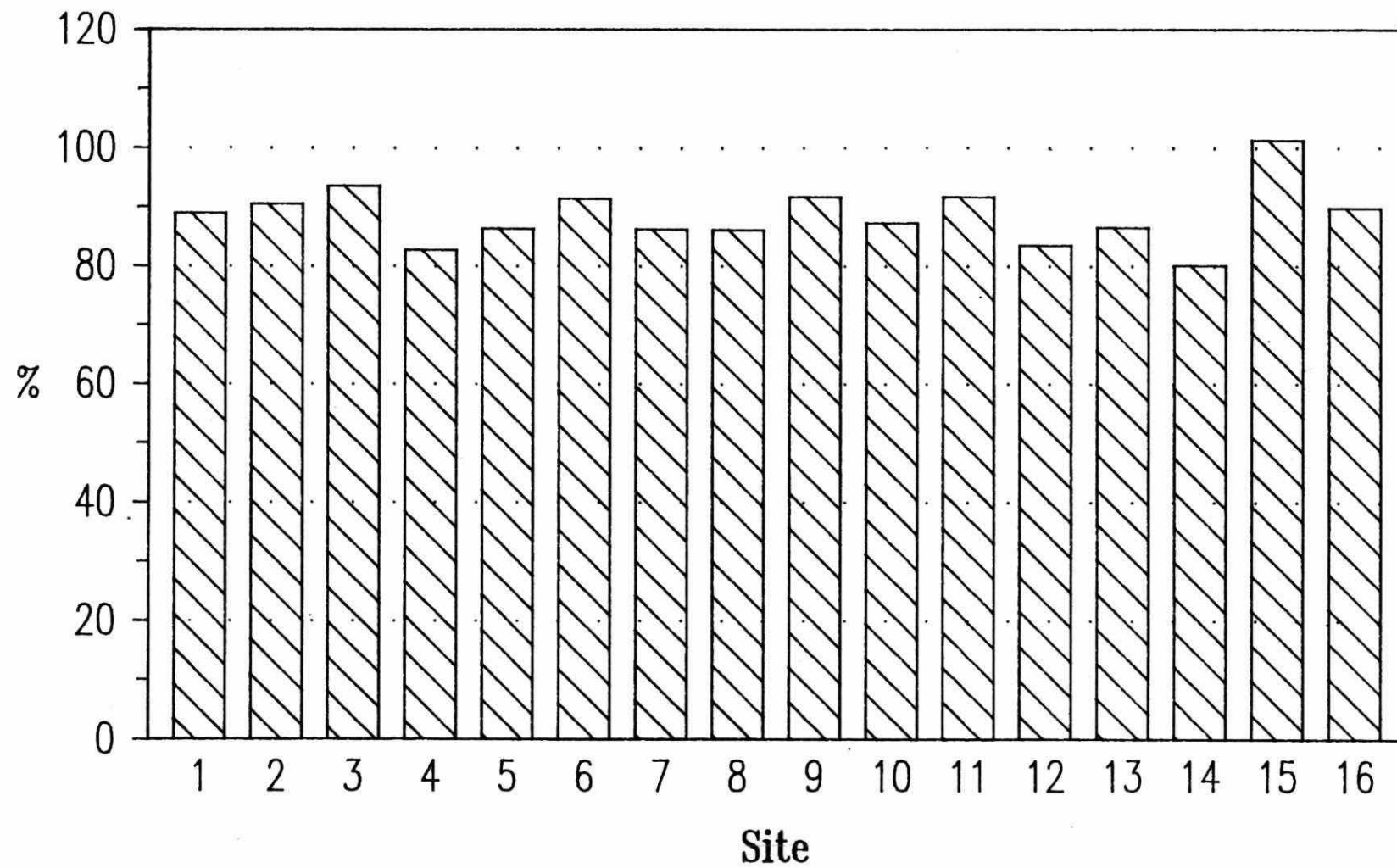


Fig. 30 Histogram of Sampling Efficiencies  
Aerochem Metric Sampler 1981

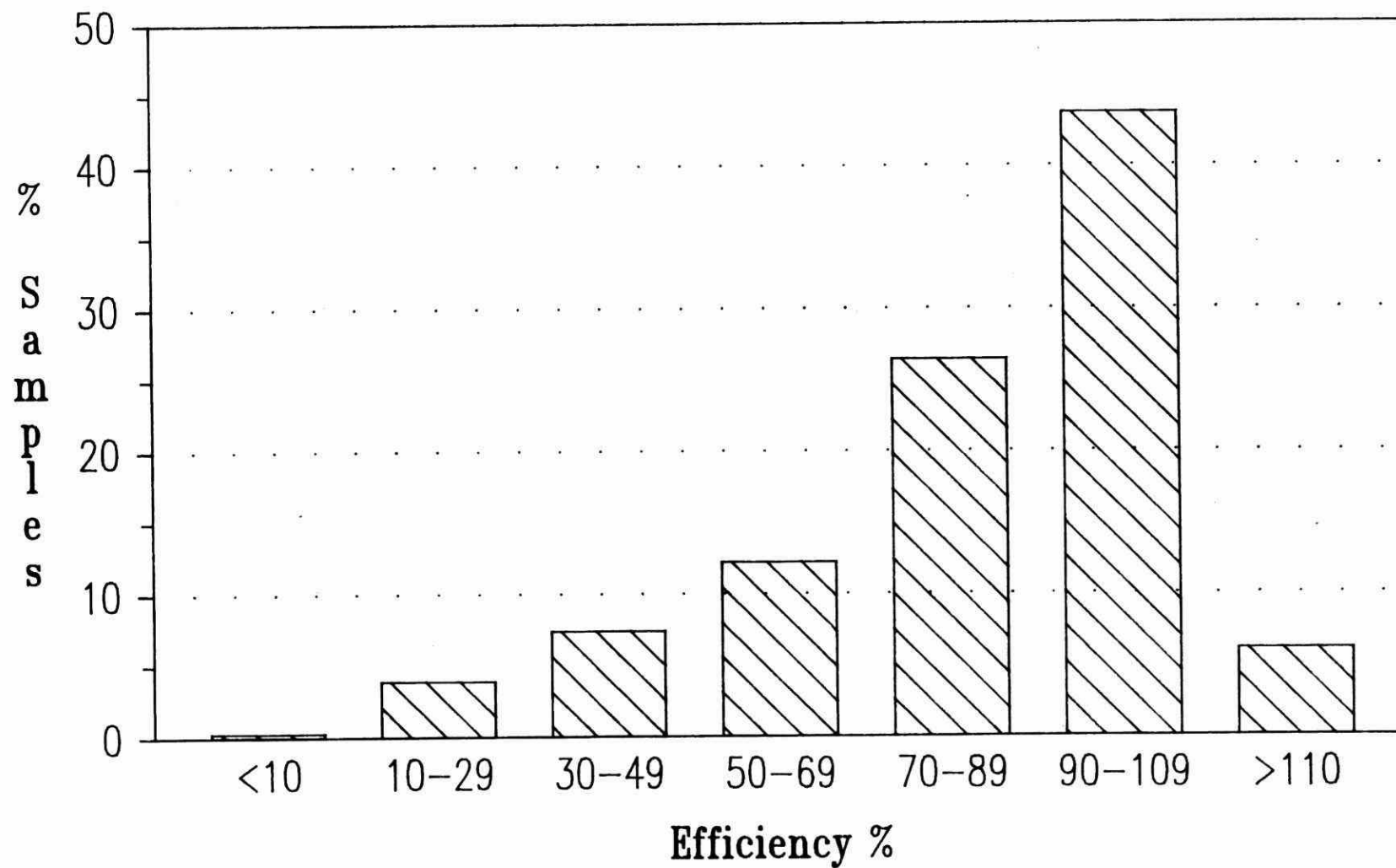


Fig. 31 Unreliable Results – Daily Precip. Network  
1980–81

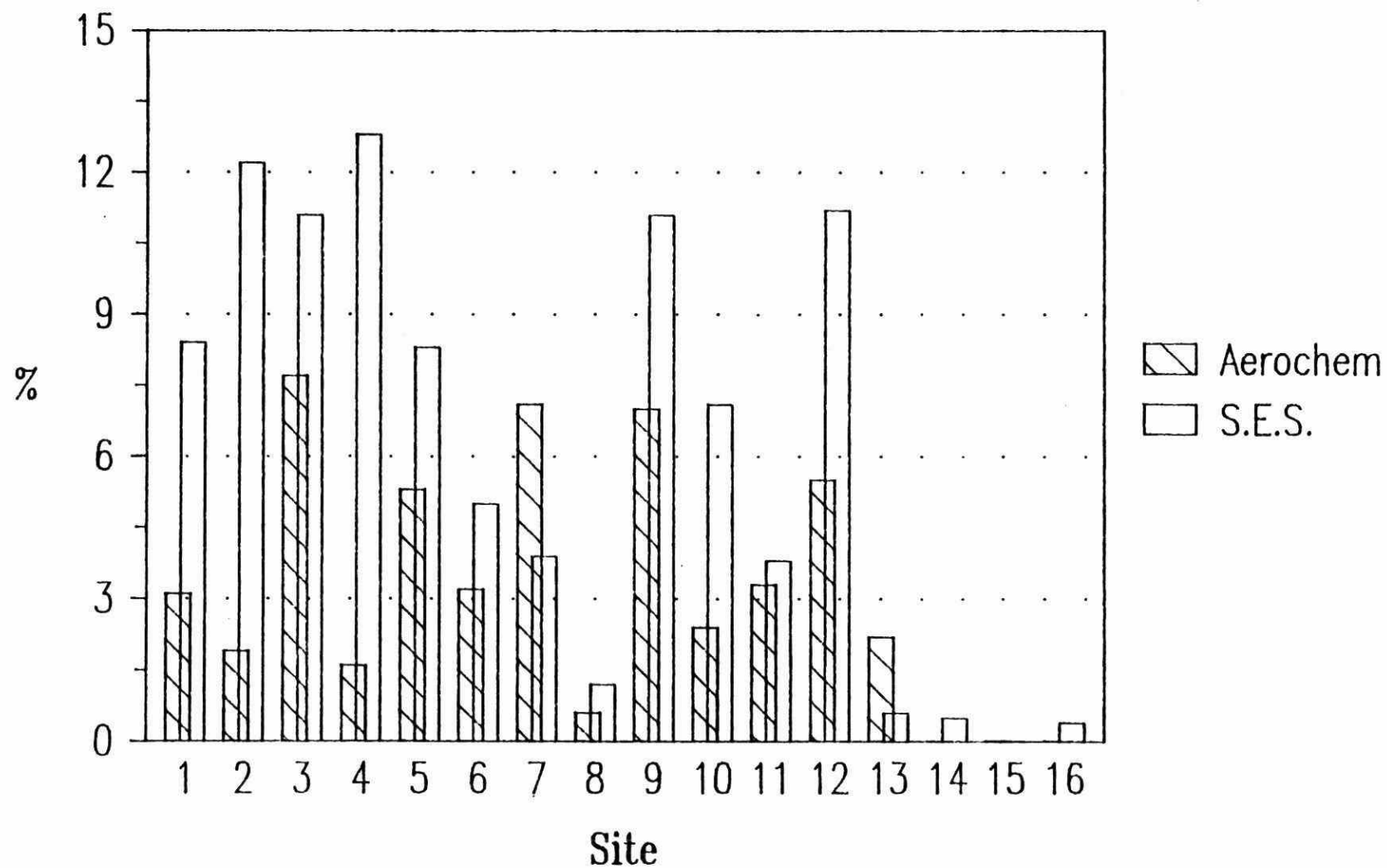




Fig. 32 Unreliable Results Vs. Region - SES Sampler  
1980-81

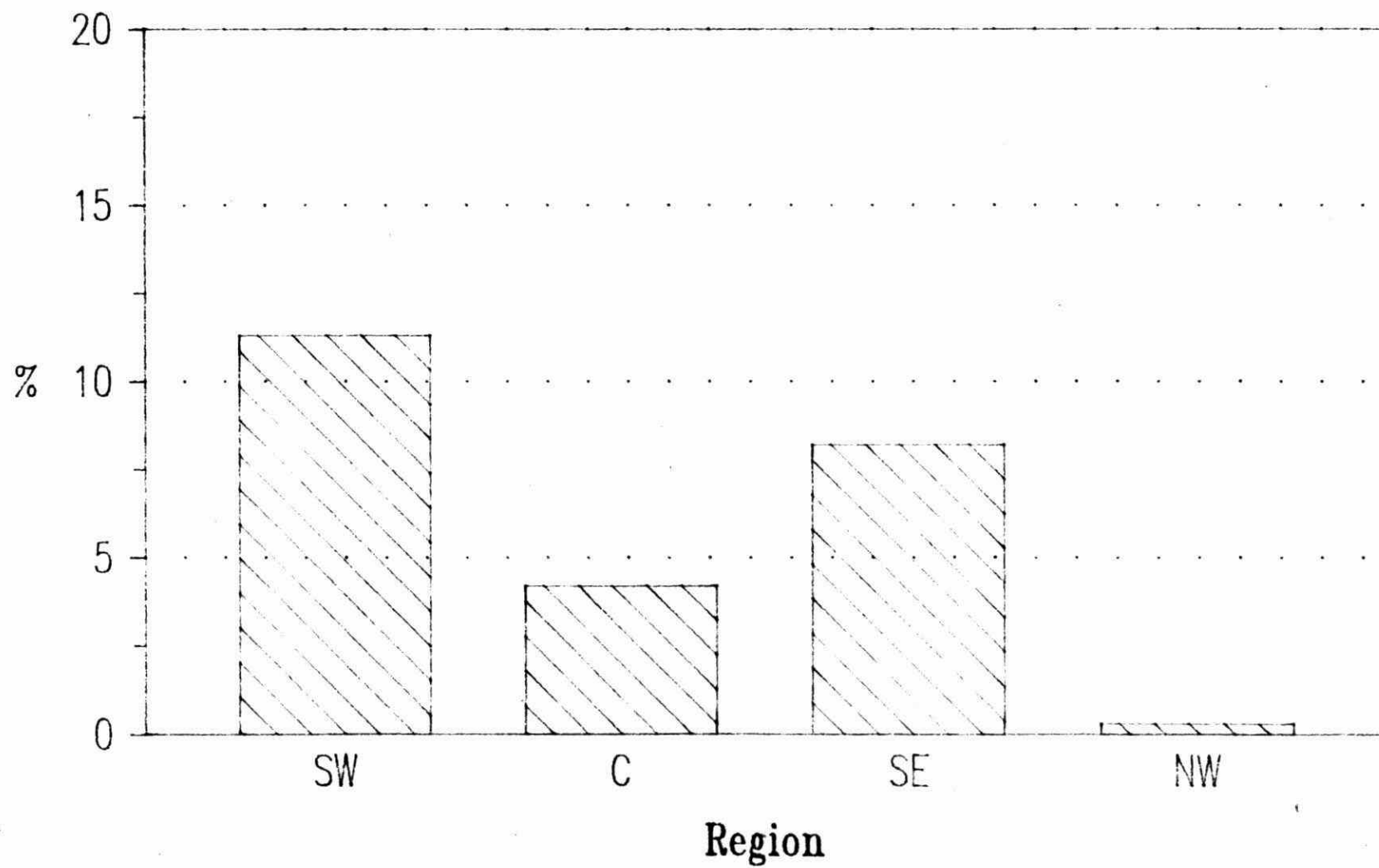


Fig. 33 Data Recovery – Daily Air Sampling Network  
1980-81

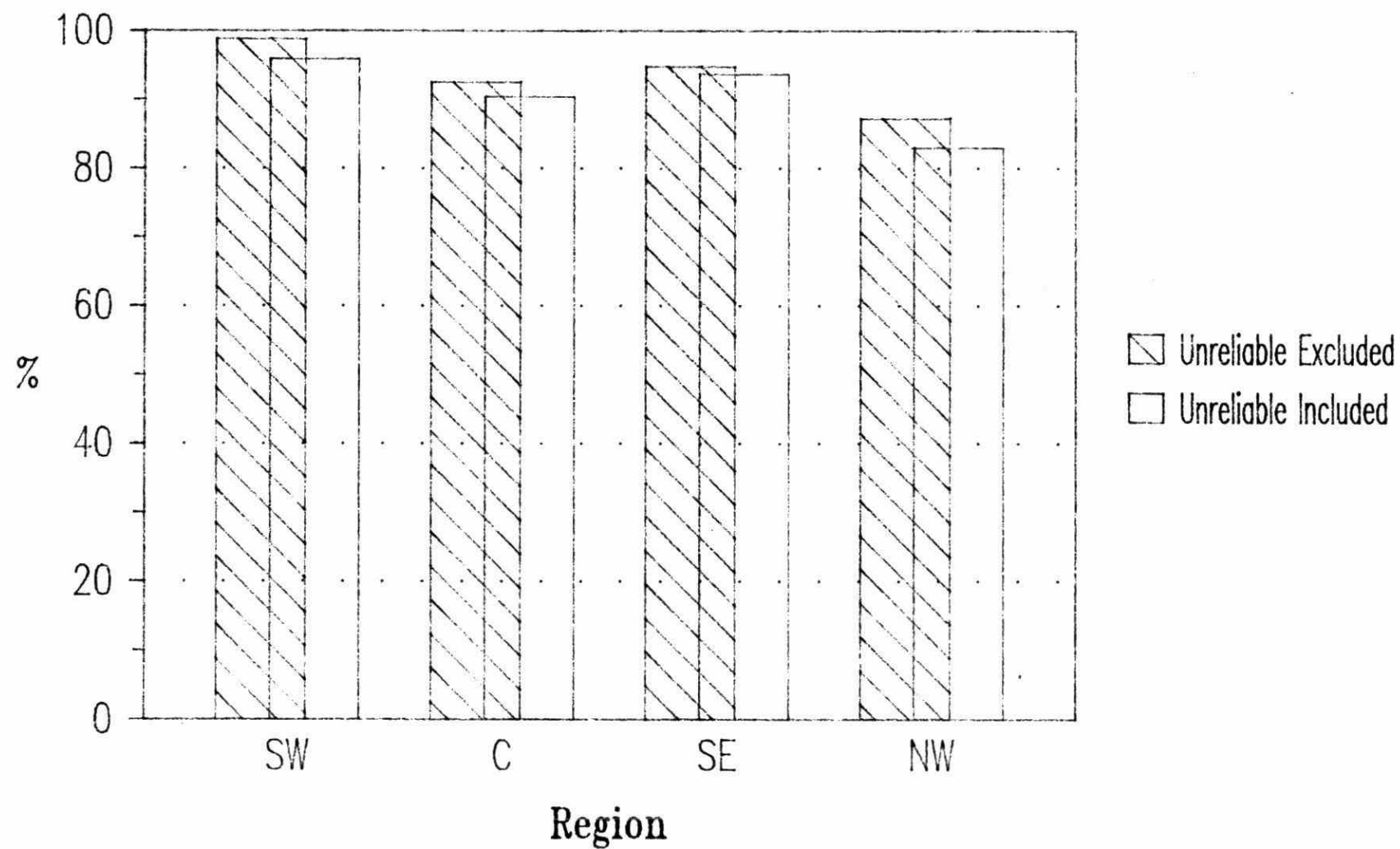


Fig. 34 Histogram of Total Air Volumes  
Daily Air Sampling Network 1980-81

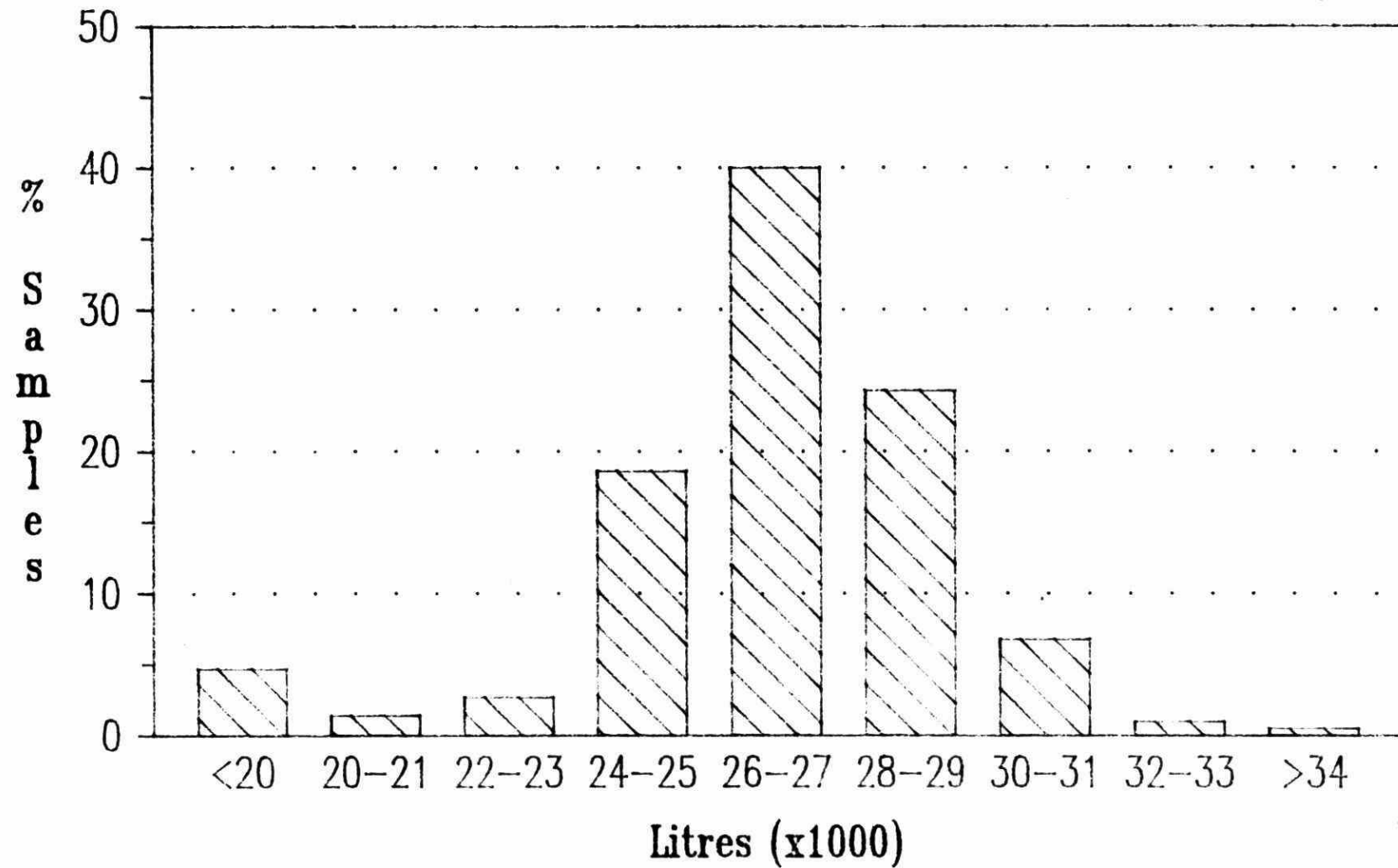


Fig. 35 Geometric Means Vs. Site  
Daily Air Sampling Network 1981

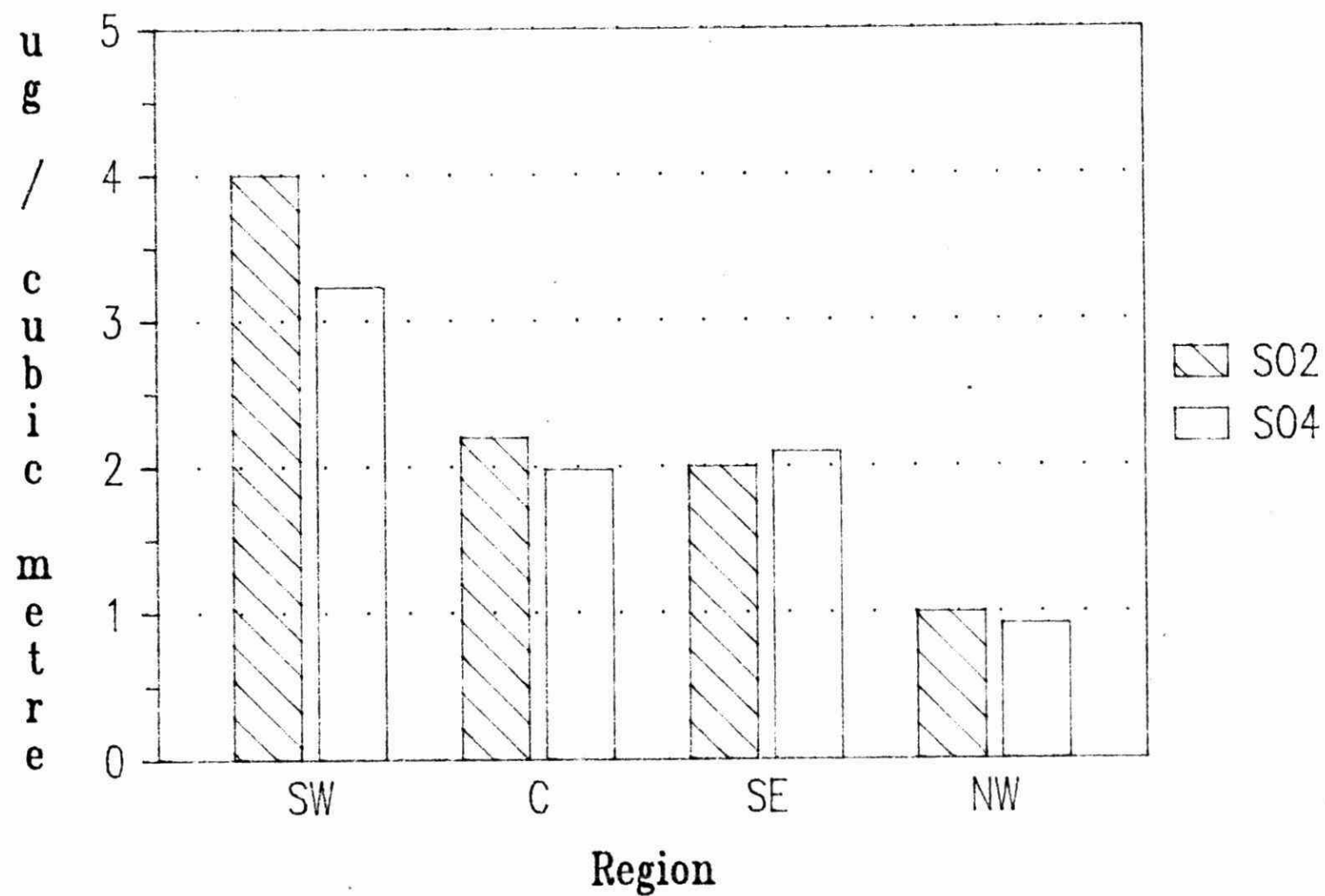


Fig. 36 Geometric Means Vs. Site  
Daily Air Sampling Network 1981

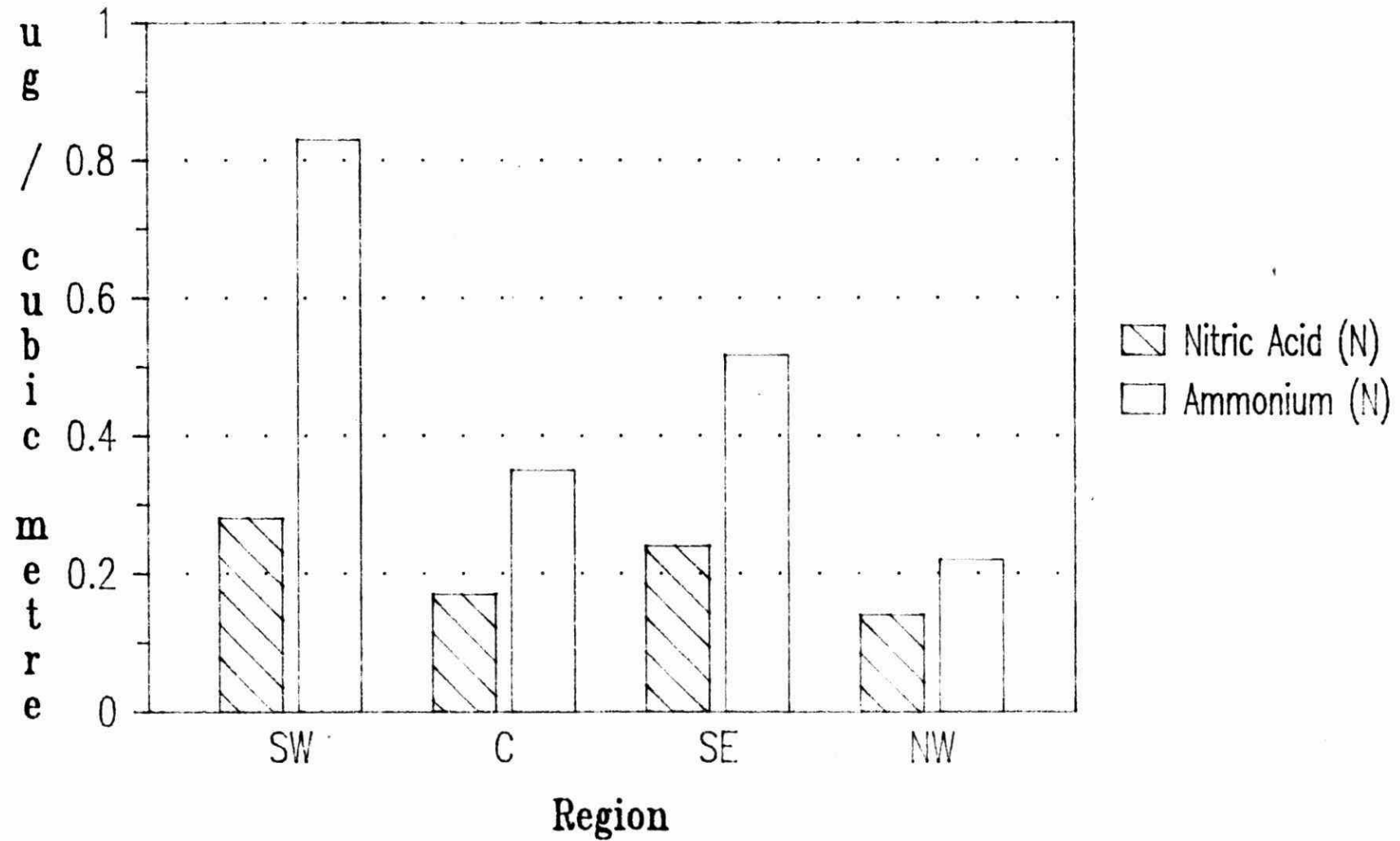
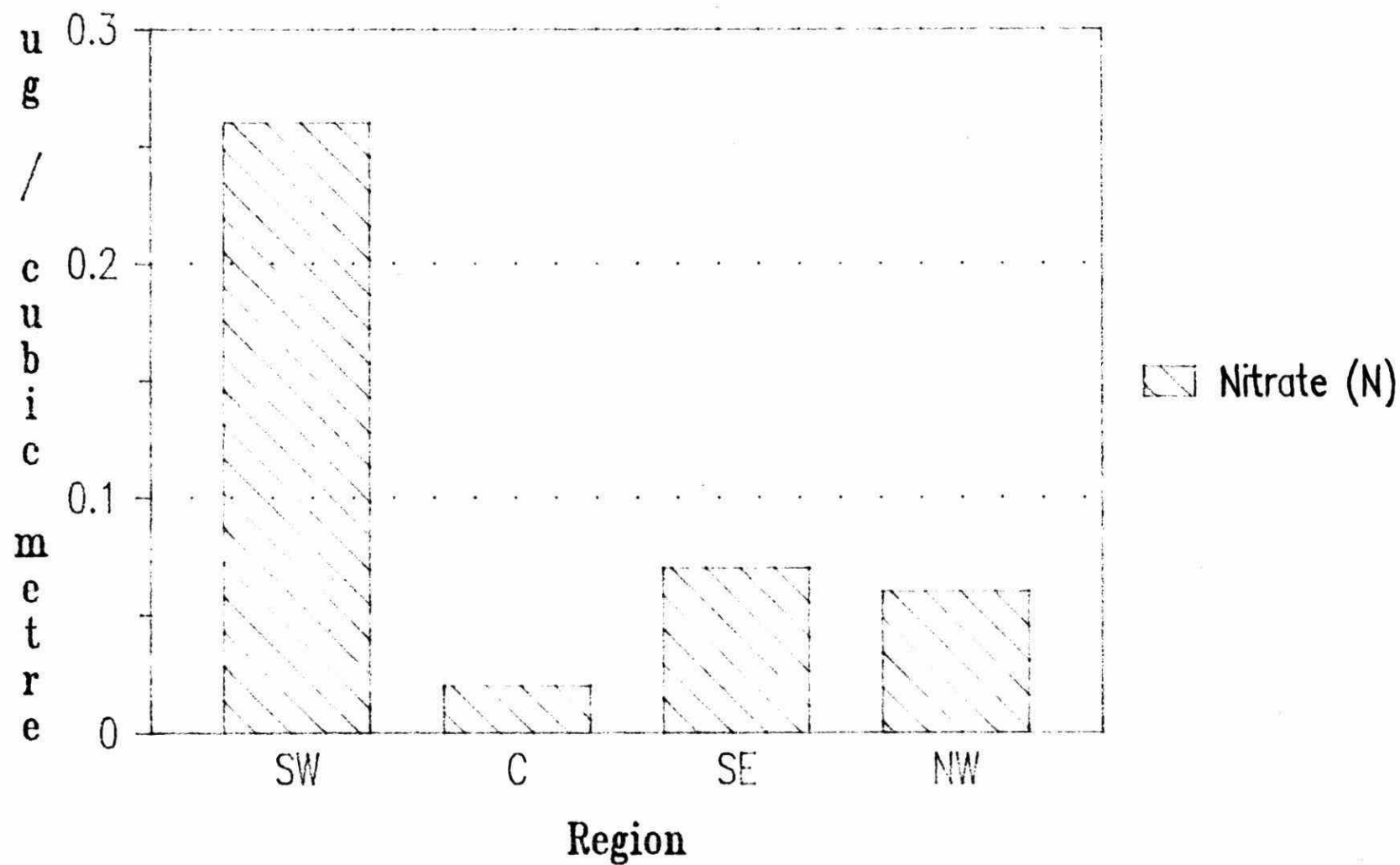


Fig. 37 Geometric Mean (Nitrate) Vs. Site  
Daily Air Sampling Network 1981



TD  
195 5.4  
06  
837  
1985